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Movement of Selected Metals, Asbestos and Cyanide in Soil: Applications to Waste Disposal Problems

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EPA-600/2-77-020
April 1977

MOVEMENT OF SELECTED METALS, ASBESTOS, AND CYANIDE IN SOIL:
APPLICATIONS TO WASTE DISPOSAL PROBLEMS

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report presents a discussion of the physical, biological and chemical reactions that affect the movement of certain hazardous substances in soils. The information is applicable to the problem of safely disposing of wastes on land.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

PREFACE

Much solid waste, whether transported by air, water, or man's activities, reaches the soil and interacts in a way characteristic of the particular environment in which it deposits. With such an explosive increase in quantity and variety of wastes paralleling the bulge in human population, the potential pollution hazard to the quality of surface and underground water as well as to the food-producing soil itself has reached serious proportions.

The soil is a dynamic system where conditions are constantly changing and where numerous reactions are taking place at any one time. The great number of attenuation mechanisms which are operative when trace contaminants from wastes are put on or into the soil can be qualitatively identified with reasonable assurance, but quantitative data relating to specific mechanisms are not available. Such a lack, however, does not make it impossible to develop a workable program for controlling potentially hazardous pollutants. The soil can be treated as a muscle where work is performed which can be measured with some degree of precision, even though not all the muscle enzymes and mechanisms of input are identified and quantitized.

There is no doubt that additional research will refine and even alter some of the concepts put forth in this report. However, this information is presented as the best available in November 1974 for guiding management of solid and hazardous waste disposal on land and research on the problems associated with such disposal.

Nic Korte, Elvia Niebla, Bruno Alesii, Colleen McCarthy, and Joe Skopp have been responsible for the laboratory progress of the Arizona research program. I am indebted to them, particularly, and to others attached to

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Supplements to this publication will be issued as additional information on the subject becomes available. Critical comments, suggestions for improvements in format and presentation, and citations of pertinent literature that was omitted or that has recently been published would be appreciated. Address such comments to:

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ABSTRACT

This report presents information on movement of selected hazardous substances in soil which can be applied to problems of selecting and operating land disposal sites for wastes containing arsenic, asbestos, beryllium, cadmium, chromium, copper, cyanide, iron, lead, mercury, selenium, and zinc. The information is based on a literature review, laboratory studies of movement of hazardous substances through soil in municipal landfill leachate, and the author's experience in soil science and waste disposal.

In addition to a discussion of the soil and waste-related factors to be considered in selecting and managing disposal sites for minimum migration hazard, the report also presents general information on soils and geological materials and specific information on the chemistry of the selected hazardous substances which is relevant to an understanding of their migration in soil. Critical information gaps are identified, particularly as regards the chemistry and soil adsorption behavior of mixtures of several hazardous substances in the presence of high concentrations of other organic and inorganic solutes, a situation commonly encountered in leachates from municipal and hazardous solid wastes. In spite of these information gaps, it is concluded that waste disposal practice can be improved by application of present information. The report contains 250 references and a bibliography of 81 related citations.

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SECTION I

SUMMARY

A critical review of the literature pertinent to biological, chemical, and physical reactions and mechanisms of attenuation (decrease in the maximum concentration for some fixed time or distance traveled) of selected elements -- As, Be, Cd, Cr, Cu, Fe, Hg, Pb, Se, and Zn -- asbestos and cyanide in soil systems is presented.

A "state of the art" on migration rate through soil of potentially hazardous pollutants contained in leachates generated from solid waste and wastestream disposal was developed. This presentation originated from (a) a critical review of the literature, (b) ongoing research at The University of Arizona, and (c) the author's best knowledge and expertise in the area of soil and water sciences.

Only a limited amount of information concerning the attenuation in soils of the 10 selected elements, cyanide, and asbestos originating from solid wastes or any other sources is available. From the standpoint of practical application, the literature is still contradictory, fragmentary, and confusing.

Despite the limited usable data in the literature and only partially completed research program at The University of Arizona, certain guidelines have been developed which are useful for initiating a pollution control program for wastes disposed-of on land.

Throughout the report, needs for supporting research data are suggested.

Solutions (leachates) containing hazardous constituents must migrate through soil and geologic material to reach the capillary fringes of underground water reservoirs. Because the soil is a far more reactive and dynamic system than geologic material, the soil's capacity to immobilize and retain (attenuate) pollutants is far greater than that of geologic materials.

Numerous factors have been suggested as influencing mobility of elements in soils. Among those most frequently mentioned are: Physical -- texture (particle size distribution), structure (pore size distribution), bulk density, temperature, moisture regime, aeration; Biological -- aerobic and anaerobic microbial transformations of inorganic and organic substances, addition of certain microbial products to the system, removal of inorganic ions from solution by, and transitory immobilization in, microbial tissues; changing of the quantity of an element in the soil by such mechanisms as volatilization; Chemical -- pH or hydrogen ion activity, oxidizing/reducing conditions, lime, organic matter, concentration of ions or salt, and certain hydrous oxides.

Under appropriate conditions any of these factors could become dominant and exert the controlling influence on mobility. However, in general, the following will be the most significant:

1. Soil texture or particle size distribution (sand, silt, and clay).
2. Pore space distribution (soil structure, bulk density, compaction, etc.) is closely related to Number 1, above.
3. Content and distribution of Fe, Al, and Mn hydroxy oxides and oxides in soil and coating particles.
4. pH (pH of soil and leachates and buffering capacity).
5. Reduction/oxidation potential in the soil in micro- as well as macro-pores (anaerobic and aerobic, oxic and anoxic conditions).

6. Soil organic matter and amount and concentration of organic constituents in the wastes which may become an energy source for microorganisms.
7. Concentration of hazardous ions.

These are not listed in order of importance because the intensity with which a factor is expressed will determine its influence, relative to other factors, on mobility. Overlappings and interactions among physical, biological, and chemical factors are to be expected as a rule, not as an exception.

One of the most critical factors in attenuation of the selected hazardous constituents in soils is pore size distribution. Since this will vary significantly even at short distances within a single soil type (or series), a valid laboratory evaluation of the suitability of a disposal site can be made only on disturbed soil and geologic material where minimum heterogeneity is established. Disturbing the soil is to be viewed as a very favorable and even an essential practice in land disposal of wastes because such disturbance will increase attenuation by increasing the number of smaller pores, reduce channeling, and improve contact conditions with soil particles.

Among the many soil parameters studied at The University of Arizona with selected soils representing seven major soil orders in the U.S., attenuation and mobility were significantly correlated with particle size distribution (texture) and the amount of extractable iron, probably dominated by hydrous oxides of Fe. Because texture varied so widely among the soils, an evaluation of soil characteristics other than Fe content may not have been made satisfactorily.

Based on information in the literature, the 12 selected constituents may be grouped as follows with respect to mobility in soil under aerobic conditions:

Mobility Class	Element	Comments
I. <u>Relatively mobile</u>		
	Cyanide - CN^-	Not strongly retained by the soil.
	Selenium - HSeO_4^- & SeO_3^{2-}	Not strongly retained by the soil, at normal pH levels.
II. <u>Moderately mobile</u>		
	Iron } Zinc } Lead } Copper }	{ Absorbed more strongly by the soil in the order of $\text{Cu}^{++} > \text{Pb}^{++} > \text{Zn}^{++} > \text{Fe}^{++}$. Stability for complexes of any given type should be increasing in the order of $\text{Fe} > \text{Zn} > \text{Pb} > \text{Cu}$.
	Beryllium - Be^{++}	
III. <u>Slowly mobile</u>		
	Arsenic - H_2AsO_4^-	Mobility similar to phosphorus.
	Cadmium - Cd^{++}	Forms insoluble precipitates in oxidizing conditions.
	Chromium - Cr^{+++} (or Cr^{+6})	Forms insoluble precipitates in oxidizing conditions.
	Mercury - Hg^{++}	Retained in the surface layer of most aerated soils.
	Asbestos - $< 2\mu$	Particles less than 2μ , are retained in surface layer of soils like clay.
IV. <u>Immobile</u>		
	Asbestos - $> 2\mu$	Particles $> 2\mu$, or greater than clay size are retained on the surface of soils.

Based on the results to date (1974) at The University of Arizona using municipal landfill leachate as the transporting medium the relative mobility of eight selected constituents under anaerobic conditions is as follows:

Soil Series	Element in Leachate
<u>Acid Soils</u>	
Ava	
Kalkaska	
Wagram	Zn, Cd, As, Cr, Se, Cu
Davidson	Be Pb
Molokai	In order of decreasing mobility →
Chalmers	
<u>Neutral to Alkaline Soils</u>	
Anthony	
Fanno	
Mohave (limy)	Cr, As, Se, Cd, Be, Cu
Mohave	Zn Pb
Nicholson	In order of decreasing mobility →

An expected grouping of the soils for immobilization of the selected elements in municipal landfill leachates under anaerobic conditions is as follows:

Mobility Class	Texture	Soil Series	Order
I. Strongly immobilizing	clay	Molokai	Oxisol
	silty clay	Nicholson	Alfisol
II. Usually strongly immobilizing	silty clay	Chalmers	Molisol
	loam		
	clay	Davidson	Ultisol
	clay	Fanno	Alfisol
	sandy clay	Mohave	Aridisol
	loam	(limy)	
III. Moderately immobilizing	silty clay	Ava	Alfisol
	loam		
	sandy loam	Mohave (lime free)	Aridisol
IV. Weakly immobilizing	sandy loam	Anthony	Entisol
	sand	Kalkaska	Spodosol
	loamy sand	Wagram	Ultisol

SECTION II

INTRODUCTION

There is no doubt that almost all waste materials, sooner or later, reach the soil and interact with soil constituents in a way characteristic of the particular habitat in which they deposit. Since air, rivers, and streams are only vehicles for waste transport, and sensitivity over what enters the ocean is keen, the soil continues to be the primary means of mass disposal. The soil is an experienced "old-timer" at effective digestion and disposal of plant and animal wastes. Recently, however, because of the quantity and variety of wastes, and variations in methods of disposal, the leachates from land disposal sites are presenting a potential threat to the quality of surface and underground water as well as to the soil itself. In view of this threat, individuals from industry and local, state, and federal government are asking for answers to questions about the best methods of disposing of wastes on land.

To speculate in the absence of at least some available data for background carries a certain tag of professional hazard. Yet, not to speculate at all carries an even worse penalty of stagnation in professional progress. This report on the potential for migration of twelve hazardous substances in soil takes the middle road between complete speculation and the conservative, traditional scientific approach. Having enjoyed many years of university and federal research and college teaching, I do not welcome having to take this middle position. On the other hand, when confronted with the growing demand by industry and society for some guideline ... any guideline ..., planning for the safe disposal of wastes must be initiated; my conscience dictates a program of action. This action is in the form of a report which presents an interpretation of the literature along with our best knowledge

of the major biological, chemical and physical reactions in soil of some potentially hazardous pollutants. Since this information relates to pollutants which are already in solution, this report applies both to liquid wastes and the leachates from solid wastes disposed of on land. The constituents to be reviewed are: arsenic, asbestos, beryllium, cadmium, chromium, copper, cyanide, iron, lead, mercury, selenium, and zinc.

The many threads of the "state of the art" of migration and attenuation of these constituents must be pulled together as a point of departure for future research planning as well as for initiating a functional land pollution control program for protecting the quality of our environment and insuring the future survival of man. To meet these objectives most effectively, research information available in the literature as of 1974 and that currently developed at The University of Arizona have been combined in this report. The result is a hybrid of a review and a research report.

The specific objectives of this work were to (a) provide a critical review of the existing literature concerned with biological, chemical and physical reactions of certain hazardous materials in soil systems, with emphasis on the migration potential of these materials through soils; and to (b) map out areas for future research aimed at providing a base for development of pollution-control procedures and guidelines regarding land disposal of the designated hazardous materials.

This review-report is presented in eight sections. Section I provides a summary for transmitting the gist of the report for those who do not have a need to delve deeply into the subject matter and the multisciences bearing on molecular and ion migration through the soil.

Section II is the Introduction.

In Section III, some recommendations for disposal of wastes containing the selected hazardous constituents which may be solubilized and appear in aqueous leachates are discussed. The impact of the ongoing research at The

University of Arizona is incorporated most distinctly in this part.

In Section IV, background information on the general characteristics of soils and geologic material as may influence the migration of hazardous substances in soils is given. It is prepared principally for the uninitiated in soil science and geoscience. The natural content of the 12 hazardous constituents in soil is also given in this section.

In Section V, the potential for migration of the hazardous constituents through soil is discussed in broad terms and an estimation of the relative rates of mobility through soils of these constituents is presented. The attenuation classification of soils and migration potential classes of hazardous materials are based largely on work with metals in the matrix of municipal landfill leachate. Results may differ if the metals are carried in a different matrix or were present in higher concentrations, as, for example, leachates from some industrial waste streams. A discussion of attenuation mechanisms is included in this section.

Section VI discusses some of the chemistry of the 12 hazardous constituents. This information is presented not as having direct application to disposal problems but as forming a basis for understanding the attenuation mechanisms discussed in Section V.

The literature on trace and heavy elements as it may relate to any aspect of the soil is dominated by the following fields of interest to the almost complete exclusion of other fields.

1. Concentration evaluation of trace elements necessary as nutrients for plant growth in soils.
2. Uptake of trace nutrient elements from soil by plants.
3. Chance uptake of a few heavy elements from soil by plants, as related to growth inhibition and toxicity.

4. Chance uptake by plants of trace and heavy elements contained in sewage effluents, sludges, and municipal composts applied to soils.
5. Concentration evaluation of trace and heavy elements in bottom mucks and muds of lakes, streams, and seas where waste disposal has occurred over a period of time.
6. Surface soil contamination from industrial stack gases and particulates, automobile emission, industrial substances, etc.

The geochemist has focused attention, almost wholly, in areas of element behavior not closely related to soil or soil problems. Accumulation mechanisms of indefinite forms of elements often occurring in soils have been avoided as a field of study.

Soil scientists also have failed to consider trace and heavy elements in the broader aspects of soil interaction except as essential plant nutrients or, to a limited extent, as toxic factors in normal plant growth. The agricultural approach has dominated to the complete exclusion of all other approaches, particularly pollution control.

Certain terms used in this report have such a wide variety of meanings that they require defining. Some of the most conspicuous ones are:

Absorption - is confined to biological uptake of elements and constituents.

Adsorption - relates to a physico-chemical process of holding or the immobilization mechanisms against extraction by salt solution.

Adsorption complex - The group of substances in soil capable of adsorbing other materials. Organic and inorganic colloidal substances form the greater part of the adsorption complex; the noncolloidal materials, such as silt and sand, exhibit adsorption but to a much lesser extent than the colloidal materials.

Attenuation - Attenuation is defined by looking at the movement of a pulse of a solute through a soil. As the pulse migrates, the maximum concentration decreases. Attenuation can then be defined as the decrease of the maximum concentration for some fixed time or distance traveled.

Fixation - Fixation is defined for use in this report as that portion of trace contaminant retained against salt extraction. (Some investigators, particularly those in the plant sciences, use another criterion, i.e., that portion of constituent retained against acid extraction.) The Soil Science Society of America (1964) definition is: "The process or processes in a soil by which certain chemical elements essential for plant growth are converted from a soluble form to a much less soluble or to a non-exchangeable form; for example, P "fixation." Contrast with N "fixation."

Hazardous Substance - A substance which may cause or contribute to an increase in mortality or serious illness on account of its toxicity, persistence, mobility, or potential for accumulation or concentration in tissue. Such substances may be harmful even in small quantities. See, for example, the allowable concentrations of metals in the Interim Primary Drinking Water Standards (Federal Register, March 14, 1975, 40(51):11994). The hazardous substances considered in this report were selected from the pollutants covered by the Clean Air Act and the Federal Water Pollution Control Act, reasoning that tightening restrictions on discharge of these into air and water must inevitably lead to their increased disposal on land, the only remaining sink for wastes. Iron, though not strictly hazardous, was included because it is known to be one of the major pollutants in leachates from municipal landfills.

Heavy Metals - In the chemical literature the term "heavy metals" generally refers to those metals which have densities greater than 5.0.

Landfill Leachate - originates primarily from natural rainfall indigenous to the climate in which the landfill is located. It accumulates as rain

wets the landfill, infiltrates the solid waste pore spaces, and finally occupies the lower levels of the landfill varying in depth according to the balance between infiltration rate of the surrounding soil and/or geologic material and intensity of the rainfall. Biological transformations within the leachate are dominated by anaerobic processes. Landfill solid waste may be municipal (residential wastes), industrial (primarily from chemical, mining, agricultural, food-processing, or forestry processes). The landfill leachate used in The University of Arizona research program originated from typical municipal solid waste.

Sorption - relates to loosely as well as strongly fixed ions or molecules by the soil constituents. A host of mechanisms is involved.

Trace Elements - These elements, especially metals, are used by organisms in minute quantities but nevertheless are believed to be essential to their physiology. (In a looser sense, the term has been used to designate elements with no known physiological function.) More recently it has been used also to refer to elements which, though present in only minute quantities, are toxic to living systems.

Trace Contaminants - Trace contaminant in this text refers to the ten elements listed (As, Be, Cd, Cr, Cu, Fe, Pb, Hg, Se, Zn), asbestos, and cyanide. They may or may not be essential for plant growth; but, if present in the soil solution in great enough concentration, are absorbed by, and toxic to, plants.

In this report "trace elements" will refer to As, Be, Cd, Cr, Cu, Fe, Hg, Pb, Se, and Zn. "Heavy metals," "heavy elements," "transition elements," in this report, will refer to As, Cd, Cr, Pb, Se, and Hg even though As and Se are not transition series. Asbestos and cyanide will be considered potentially hazardous pollutants along with the elements just listed but will be referred to as substances, materials, or constituents, as well as by their given names.

The soil is a dynamic system where conditions are constantly changing and where numerous reactions are taking place at any one time. The great number of attenuation mechanisms which are operative when trace contaminants are put on or into the soil can be qualitatively identified with reasonable assurance, but quantitative data relating to specific mechanisms are not available. The lack of such data, however, does not make it impossible to develop a workable program for controlling the spread of potentially hazardous pollutants from land disposal sites. The soil can be treated as a muscle where work is performed which can be measured with some degree of precision, even though not all the muscle enzymes and mechanisms of input are identified and quantitized. This type of research program, currently underway at The University of Arizona, Tucson, is described in the appendix. Attenuation predictions are best made on a relative basis, e.g., by comparing one element with another and by comparing various soils. Predictions derived from such laboratory data provide maximum attenuation information for any given element. Attenuation in undisturbed field soil may be less because of differences in pore size distribution, a more "open" soil structural condition, and other possible soil physical variations.

There is no doubt that additional research and experimentation will refine and even alter some of the concepts put forth in this report. However, guidelines for safe disposal of wastes on land are needed now and this report presents the best information available as a basis for their formulation.

SECTION III

SOIL AND WASTE RELATED FACTORS TO BE CONSIDERED IN SELECTING AND MANAGING DISPOSAL SITES FOR MINIMUM MIGRATION HAZARD

The information presented here has its origin in a synthesis of data obtained from the literature review, the ongoing University of Arizona research program, and from the author's experience. This is a preliminary attempt to provide information useful in the selection of land disposal sites and in the management of existing disposal sites so as to minimize the hazard of migration through soil. This part contains two broad subsections. The first is a discussion of some factors affecting migration with emphasis on how the waste or soil at a particular site can be managed to minimize migration. The second contains a detailed listing and discussion of the chemical and physical properties and attenuation ratings for soils used in a laboratory study of pollutant migration in municipal landfill leachate; it is intended to aid in selecting the best of several soils for attenuation of pollutants. The information from both subsections is repeated and explained in greater detail in other parts of this report.

FACTORS AFFECTING MIGRATION RATE

The many factors affecting migration rate have been sorted out to identify those most often dominant in movement of the 12 selected potentially hazardous pollutants (trace contaminants) through soil. Before discussing specific factors, two important general conditions should be mentioned.

The first is that the soils themselves contribute to the sum of the materials, including the 10 elements listed as trace contaminants, that move through the soils, finally entering underground water or lodging in the soil as insoluble or slowly soluble compounds. Elements in these compounds may

be re-released by man's activities, specifically, by the disposal of acidic or acid-forming wastes on the soil. In some instances, particularly newly developed agricultural lands in arid regions which have not been previously leached, the natural migration in itself may be sufficient to pollute the groundwater beyond human use. In other instances (depending on the composition of the overburden of soil and geologic debris) the quantity and quality of such migration is of little or no significance to water quality. Climate, particularly rainfall, is a highly significant factor in natural soil pollution since it may provide the vehicle for movement or may have previously leached most of the readily soluble materials out of the soil.

The second important condition to recognize is that the soil-contaminant relationship is dynamic and time must be a consideration in any assessment. For example, ions are not permanently attached to cation exchange positions on the clay minerals. As the concentration of the ion in solution decreases or the concentration of a competing ion increases, some or all of the ions on exchange positions will be exchanged and free to migrate. Thus, as the waste or the soil environment changes, the attenuation becomes time dependent and the soil must be viewed not as a capacitor which only stores contaminants but as a parallel-connected capacitor and resistor which "leaks" at some rate which changes with time and with the forces applied to it. In this same context, while only very small concentrations of contaminants, even near the limit of detectability, may be in a mobile status, accumulation in soil and later release in significant quantities may take place over an extended period of time. Thus, very small concentrations may have to be considered significant because of the time factor.

Specific Factors Influencing Migration

There is no definite division between those factors which decelerate or accelerate migration of the trace contaminants through soils. The influence depends on the intensity with which all factors are expressed in the soil. A factor which may decelerate or attenuate a constituent in one soil may have either no effect or an opposite effect in another soil. Moreover,

a factor which may inhibit movement of one element may have no influence on the movement of another element.

The following listings, however, are based on what may be considered as general or broad trends suggested in the literature. The factors are discussed not necessarily in the order of importance because relative importance depends on the other factors present in the soil.

1. Hydrogen ion activity (pH)

- a. Soils - Except for selenium, chromium, and some valency states of arsenic, attenuation (decelerated migration) may be expected to be greater in soils of neutral to alkaline pH values.
- b. Aqueous wastes - An aqueous solution containing some level of one or more of the trace contaminants originating from solid or liquid wastes deposited on land. The soil is very well buffered but prolonged discharge of highly acidic (pH below 2.0) or highly alkaline solutions (above 8.5) alter the soil pH and cause the release of natural soil constituents (among which will be some of the trace contaminants) for migration. This effect is most pronounced in sandy soils with no free lime and least pronounced in fine-textured calcareous soils. Highly alkaline aqueous wastestreams keep many of the contaminants immobilized until the pH of the soil rises above 8.5. Except for selenium, chromium, and possibly some valency states of arsenic the more acidic the soil-waste medium, the greater is the solubility of the constituents both in the soil and in the liquids associated with the waste. Consequently, as the acidity increases from neutral (pH value decreases) the attenuation tends to decrease, i.e., migration accelerates.
- c. Selenium, arsenic, and chromium - The literature is quite clear in that selenium is more available to plants when the soil is alkaline, Brown and Carter (1969). It may be inferred that it will also be more mobile under these conditions. Research at The University of Arizona has indicated, in general, that Mohave soil which is high in native lime retards migration of the trace elements studied. However, Se, As, and Cr have been unexpectedly mobile through this soil.

With Se, this is probably due to the high pH stabilizing soluble selenates in the soil solution. In the case of As and Cr, no such corroboration has been found in the literature. However, on a quantitative basis both are much more mobile in alkaline soil than was expected. In a separate experiment, Cr was leached through a layer of lime and there was no observable difference between the presence or absence of the lime layer over a sandy soil. In contrast, the difference between lime and no lime was very great for Ni and Cd.

- d. Management - To minimize migration, the soil, or the liquids associated with the waste, or both can be managed to maintain neutral to slightly alkaline conditions by adding agricultural limestone or other liming material and by excluding or pretreating acidic wastes. In agriculture, remedying plant diseases due to an excess of soluble trace metals is done by raising soil pH to decrease the solubility/availability of the trace metal. Likewise, in the mining industry, pH control is a well established practice for treatment of trace metal-bearing waste waters, Pearson, et al. (1975).

2. Oxidation/reduction (redox)

A reaction in which an electron transfer takes place is called an oxidation-reduction process. An element or substance giving off electrons is being reduced. For example, $\text{Fe}^{+++} + e \rightleftharpoons \text{Fe}^{++}$ or $\text{Ox} + ne \rightleftharpoons \text{Red}$. The intensity of the oxidizing or reducing action of a system is determined by a standard electrode placed in the solution system. The potential difference between the electrode and solution is called redox potential. Under reducing conditions, i.e., usually the absence of free molecular oxygen, chemical or biological oxygen-demanding reactions are consuming oxygen at a greater rate than it is being transported into the system. Microorganisms find a substitute for O_2 in metabolic processes. These substitutes may contain combined oxygen as nitrates (NO_3^-) or sulfates (SO_4^{2-}) or may involve electron transfer without the involvement of oxygen as with Ferric (Fe^{3+}) or manganic (Mn^{4+}) substances.

Oxidizing conditions favor attenuation as opposed to reducing conditions. The transfer of electrons need not include oxygen. Cyanide is an

exception. When it is oxidized to NO_3^- , it is highly mobile. The reduced form, NH_3^- is less mobile. Precipitates develop in anoxic landfill leachates upon exposure to air (oxic conditions). Many of the trace contaminants become a part of this insoluble residue, Korte et al. (1976).

Reducing (anoxic) conditions favor accelerated migration of heavy metals as compared with oxidative (oxic) conditions. For example, trace contaminants As, Be, Cr, Cu, Fe, Ni, Se, V, Zn, are much more mobile under anaerobic than aerobic soil conditions, all other factors the same. Water logging such as exemplified by the soil below the leachate level of sanitary landfills favors accelerated mobility of most trace constituents. The effect of aerobic (oxidizing) and anaerobic (reducing) conditions on mobility is discussed in greater detail later in this section.

When wastes are disposed-of in ponds, lagoons, or deep fills, management of redox status is not always practicable. However, in land spreading or spray irrigation operations, oxidizing (aerobic) conditions can be promoted by allowing the soil-waste system to dry between waste applications. The determination of the tendency for soils towards oxidation or reduction conditions should play a part in establishing management practices for waste and wastewater disposal sites.

3. Particle size distribution of soils

Many attenuation mechanisms involve physical and chemical reactions on surfaces. The greater the surface area available, the greater is the potential for attenuation by these mechanisms. Because of greater surface area per unit weight, finer soil materials (silts, clays, and colloids) have greater attenuating characteristics than the coarser material (sands and gravels). In general, the finer the soil texture, the less is the migration of trace constituents. One should keep in mind, however, that the soil contains a great number of colloidal species both organic and inorganic which vary several-fold from each other both with respect to ion exchange capacities and ability to hold the trace contaminants against removal by solutions of salts, acids, alkalies, etc. The

colloidal hydroxy oxides and oxides of Fe, Mn, and Al react strongly with most of the trace contaminants and retain them against exchange much more tenaciously than the clay minerals. Hydroxy oxides (Fe, Al, and Mn) coat particles such that a small amount can have a profound influence on attenuation. Whenever possible, disposal sites should be located on fine-textured soils containing significant amounts of hydroxy oxides. Alternately, disposal sites can be lined with such soils or with a clay.

4. Pore size distribution

The pore size distribution is the volume of the various sizes (diameter) of pores in a soil expressed as a percentage of the bulk volume (soil particles plus pore space). Fine-textured soils generally have a greater total volume of pore space than coarse-textured soils but the pores in fine-textured soils are usually much smaller than the pores in coarse-textured soils. Some clay soils can impede water from vertical flow almost completely because of the very small pore spaces while sandy soils, on the other hand, transmit water rapidly.

Because water in soil pore spaces is the vehicle in which soluble constituents (colloids also, but to a much lesser extent) move and because soil water travels more rapidly through larger than through smaller pore spaces, the pore size distribution of a soil has a profound influence on migration of trace contaminants. Soils with small diameter pores will restrict the migration of trace contaminants by slowing the rate of movement of water through the soil which, in turn, allows more time for the contaminants to react physically or chemically with the soil particles. Attenuation reactions proceed at some finite rate and, for the same amount of solution passed through soil, the greater amount of attenuation would be associated with the slower flow rate.

Waste disposal sites should be selected and constructed to maximize the percentage of small pores in the soil. Fine-textured soils are preferred. Any soil can be improved by disturbing it and compacting it as deeply as practical to minimize the total pore space and maximize the amount of

small pores. Disturbance and compaction are desirable not only because they will reduce the rate of flow of water through the soil but also because fresh soil particle surfaces will be exposed which may be more reactive with contaminants.

5. Lime

Because of the effect on pH and carbonate ion concentration, the presence of lime in soil, either as a result of natural soil-forming processes or man's addition retards migration of certain hazardous elements except for Se, Cr, V, and possibly As, item 1c above. Lime added in sufficient quantity to raise the pH value of soil also is particularly effective in attenuation of certain elements as indicated in item 1c. The effect of the carbonate ion generally is to decelerate migration by combining with heavy metals to form poorly soluble precipitates (e.g., PbCO_3 , ZnCO_3 , CuCO_3).

6. Organic matter

Organic matter in soils, as well as in the aqueous leachates and other wastestreams, has a generally decelerating influence on trace contaminant mobility. For example, heavy metals and certain hazardous trace elements are found at enrichment levels in sludges and at low levels in the effluent solution. In addition to organic matter's high cation exchange capacity, which holds ions temporarily, it possesses mechanisms which strongly retain heavy metals. Organic colloids retain Zn and Cd as strongly as they retain Ca. Copper, Pb, Hg, and Cr are retained more strongly than Ca. Organic matter has the capacity to form some rather insoluble precipitates with trace contaminants. Chelation, though, can undo some of the beneficial immobilization properties of organic colloids and organic acids by forming soluble compounds with trace contaminants. The organic link to the trace contaminant (complex, chelate, or precipitate), however, is limited not only by its chemical stability, but by its susceptibility to microbial attack which can release the element for chemical reaction with soil constituents and/or further microbial incorporation.

Because of uncertainty about the rate and extent of specific reactions between organic compounds and trace contaminants and uncertainty about the ultimate fate of the compounds formed, no recommendations are offered about organic matter and selection or management of land disposal sites.

7. Concentration of ions or salts

The wide variety of reactions each trace contaminant might undergo makes relative concentrations of ions very important with respect to mobility. Low concentrations of salts favor more complete attenuation by simple attachment to soil ion adsorption positions. Also, many of the trace contaminants form very insoluble precipitates at low concentration. Examples are lead, arsenate, and sulfides of Pb^{+++} and Cd^{++} .

Where concentrations of some salts are high, the effect of competing reactions can be especially important. In a leachate containing some of the hazardous pollutants in small amounts, as well as a large amount of Ca^{++} , the Ca^{++} might effectively dominate the exchange reaction to the exclusion of the trace contaminants. On the other hand, if the sulfides were also present in high concentration, the trace elements would be immobilized by precipitation.

High concentrations of certain ions can also dramatically reduce solubilities due to the "common ion" effect. A leachate high in sulfate or chloride would shift the equilibrium of those elements precipitated by chloride or sulfate far to the right or less soluble state, in what is known as "salting out."

Concentration of ions or salts may either increase or decrease attenuation depending on (a) the kinds and concentrations of ions present in the soil solution, (b) the concentration of the trace contaminant in the soil solution and the leachate from the waste, and (c) hydrogen ion activity or pH. Each case has to be analyzed separately.

No general statement about ion concentration and attenuation can be made because the subject is too complex and very little work has been done with the chemistry of high concentration-multiple ion systems. Whenever

possible, consider mixing wastes to promote formation of insoluble compounds. Be aware that attenuation observed for a given soil and concentration of contaminant in a specific waste may not be a constant; attenuation is likely to be different if another waste with the same contaminant concentration but differing composition of other substances is disposed of on that soil.

8. Certain hydrous oxides

Adsorption reactions with hydrous oxides of Fe^{++} , Al^{+++} and Mn^{++} , in general, are considered by many investigators to furnish a major mechanism for the attenuation of heavy metals in soils. The abundance of Fe, Al, and Mn in soils and their chemistry which is sensitive to slight changes in redox make them prime mechanisms for removal of trace contaminants from circulation. Some of the trace contaminants at first may be adsorbed on the surface of the hydrous oxide and later buried by the continued formation of hydrous oxides-trace metal combinations. Leeper (1972), for example, writes an equation such as:



to explain a possible adsorption reaction.

Whenever a choice is possible, soils with a significant content of hydrous oxides should be selected for disposal sites. It is suggested, as a result of preliminary data from the University of Arizona research that soils at disposal sites be treated with iron compounds to form artificial hydrous oxide coatings on the soil particles. Based on present knowledge of the role of hydrous oxides in attenuation, this approach seems promising. However, it has not been examined in detail or field tested.

9. Climate (weathering)

Climate, as expressed in rainfall and temperature, influences attenuation. Wetting and drying, waterlogging or droughting (aerobic/anaerobic) are controlled in the soil by climate. Wetting and drying generally decrease mobility of heavy metals, particularly if they occur during short

intervals of time. Warm and hot temperature conditions, as occur where lateritic (thermic) soils form (Hawaii, southern Florida), favor the formation of the hydrous oxides and oxides in soils which are important in slowing migration of trace contaminants. High rainfall may dilute the contaminant or promote its migration through soils, depending on the rate at which the contaminant can be leached from the waste.

Management of wetting-drying or converting back and forth from anaerobic to aerobic is not practicable except when wastes are disposed of by land spreading or sprinkler irrigation systems; although it is possible to control the leaching of contaminants from waste into the soil either by covering the waste to exclude rainfall or by lining the disposal site to facilitate collection and treatment of liquids that have passed through the waste. Different climatic conditions will dictate the site selection and management system chosen.

10. Aerobic and Anaerobic Conditions

Literature is not particularly helpful because little is known about movement of heavy and trace elements through soils under anaerobic or anoxic conditions.

Oxygen-stressed soil and geologic material will receive greater research attention as soil scientists shift effort more from the historical emphasis on food and fiber production to controlled waste disposal. Soils and geologic materials surrounding and below sanitary landfills and ponds and lagoons developed for animal waste disposal are highly anoxic. Deep-well injections also create anoxic waste-disposal conditions. Excessive sprinkling or irrigation of land surfaces with sewage effluents and aqueous waste streams may conceivably develop intermittent oxygen-stressed soil as a result of waterlogging and/or partial soil saturation. Even in unsaturated soil conditions a great demand for oxygen by biodegradation processes and limited access to air by filled as well as partially filled pore spaces may create areas of anaerobic microspace and reducing conditions. Thus, in waste and leachate disposal, oxygen-stressed soil and geological material are, indeed, a common and expected

situation for which special attention is required.

Mobility of heavy metals and trace elements, in general, will be accelerated in oxygen-stressed compared with oxygen-rich soil. Some of the factors which influence mobility will be briefly reviewed to illustrate how anaerobic conditions may promote mobility of some contaminants while not affecting the mobility of others.

Some characteristics of anaerobic systems are:

- a. Gas production, CO_2 , CH_4 , and H_2S predominates; other gases, as H_2 and N_2 , form in low concentrations and occur only under special circumstances, or are not significantly involved in contaminant mobility.

- 1). Methane (CH_4) - Methane is one of the most characteristic gases produced during microbial decomposition of organic compounds under anaerobic conditions. The methane bacteria are most active between pH values of 6.4 to 7.2. Below pH 6 and above pH 8 the growth rate (and gas production) falls off rapidly. Methane does not measurably affect trace contaminant mobility.

- 2). Hydrogen sulfide (H_2S) - Under reducing conditions in the absence of "free" O_2 , hydrogen sulfide is produced by reduction to H_2S in soils. Unlike CH_4 , H_2S is highly reactive with certain trace contaminants. The solubility products of some of the sulfides are:

$$\text{FeS} = 3 \times 10^{-17} - 1 \times 10^{-16}; \text{ZnS} = 1 \times 10^{-24};$$

$$\text{CdS} = 5 \times 10^{-27}; \text{PbS} = 7 \times 10^{-28};$$

$$\text{CuS} = 4 \times 10^{-36}; \text{Hg}_2\text{S} = 1 \times 10^{-45};$$

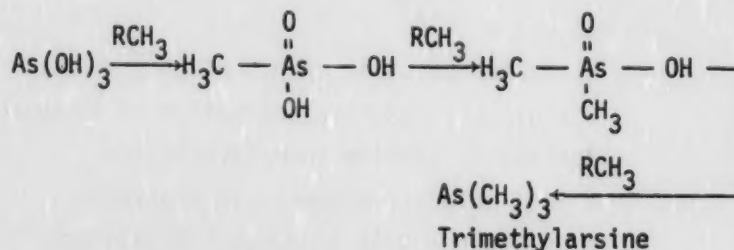
$$\text{and HgS} = 3 \times 10^{-52}$$

in a saturated solution of H_2S at $[\text{H}^+] = 1$.

This gives a relative indication of attenuation expected by sulfide formation of the various selected elements in anaerobic soils where H_2S is produced. Exceptions can occur under special circumstances.

For example, sodium sulfide may make mercuric sulfide more soluble if present in any appreciable quantity.

- 3). Carbon dioxide (CO_2) - Carbon dioxide is produced in abundance in all landfills and in landfill leachates as well as other wastes having a favorable microbiological habitat and a decomposable carbon source. This gas unites with water to form carbonic acid. Carbonic acid production reduces the pH (often as low as 5.5) and in this way contributes to accelerated migration. The abundance of bicarbonate ions (HCO_3^-) aids in keeping certain trace contaminants more soluble. Selenium and probably arsenic are not influenced as much by bicarbonate as are other trace constituents. Neither asbestos nor cyanide mobility is affected by bicarbonate or acid development. Maintenance of high CO_2 concentrations in the leachate from sanitary landfill was shown at The University of Arizona to be necessary to keep trace and heavy metals from precipitating during sampling and experimentation. Carbon dioxide production thus tends to enhance mobility, Korte et al. (1976).
- 4). Other gases - Volatile compounds of Hg and As may be produced under anaerobic conditions. Amounts of mono- and methyl-mercury produced in an anaerobic system are dependent on temperature, pH, organic loading, mercury compounds, and microbial species present (Jensen and Jernelov, 1969). Trimethylarsine also is a volatile reduction product of microorganisms. The reaction is as follows:



- 5). Hydrogen (H_2) - Small amounts of hydrogen gas evolve from anaerobic leachates. It does not appear to be an important factor in attenuation of the trace contaminants as such.
- b. Reducing conditions (redox effect) - Reducing conditions in soil promote mobility of most of the trace contaminants. Cadmium, Pb, and Hg mobility may be little affected by the lack of oxygen as compared with As, Be, Cr, Cu, CN, Fe, and Zn, which will migrate at a greater rate. Cyanide, a readily mobile constituent, will denitrify and evolve as an N_2 gas. The mobility (relative to each other) of the elements, As, Be, Cr, Cu, Fe, Zn, and asbestos and cyanide, as suggested elsewhere in this paper, for "usual" aerated soil conditions probably will not change much. Though the actual mobility of Cd, Pb and Hg will not change, their position relative to the other elements will be changed. Cyanide will be at the top and asbestos at the bottom of the list as originally, their mobility also being little altered by the presence or absence of O_2 in the soil.
- c. Organic acid production (pH effect) - Organic acids will be produced when organic materials decompose in a limited oxygen environment. This is the case in a municipal sanitary landfill or in an industrial waste landfill so long as the concentration of salts or toxic materials does not limit microbiological activity. Organic acids enhance the rate of mobility of most of the trace contaminants through the soil. Even slight lowering of the pH value of the soil solution in the region between slightly alkaline pH 8 to slightly acid pH 6 will markedly influence attenuation of most heavy elements. Asbestos, As, Se, and Probably CN mobility should not be appreciably influenced within this range. Lowering the soil pH to 3 or below (somewhat unlikely in most soils except sands and gravels), however, will greatly influence solubility of heavy and most trace elements.

Organic acids, fulvic, humic, uronic and others such as the volatile organics and carboxy ($-COOH$) and acid hydroxy ($-OH-$) radicals on large organic molecules are available to react with heavy and

trace metals. The downward movement of the trace contaminant metals through soil and geologic material as soluble metal-organic matter complexes can be of considerable importance. Fraser (1961), for example, describes Cu metal-organic-complex mobility as a factor in contaminant accumulation in underground seepage water. The organic acids produced under anaerobic conditions form chelates with many heavy and trace metals. These metals are then protected and available for accelerated movement through soils. Our knowledge in this area is still fragmentary, leaving opportunity for quantitative evaluation.

- d. Retardation of biodegradation - Anaerobic degradation of organic matter proceeds more slowly than aerobic degradation. Not only is it slower but often stops at some intermediate stage of oxidation leaving an accumulation of organic products which are free to react with the soil and constituents in the waste stream and soil solution. Slime and gum accumulation, however, tend to be less severe under strictly anoxic as compared with oxic conditions. Clogging and filling of the soil pore spaces may be expected to be less severe as compared with aerobic or partly aerobic conditions. The nature of anaerobic flora is less conducive to clogging of pore spaces than when fungi, algae and slime bacteria accumulate in the presence of oxygen. All of the anaerobic conditions tend to permit water to pass through the soil more rapidly. This effect may be counterbalanced by accumulation of unoxidized sludges, and original organic debris which would tend to have an opposing influence.
- e. Water movement not retarded by slime or gum formation - As described above, water movement may be expected to be impeded less under anaerobic than aerobic conditions. If the waste is strictly inorganic, water movement should not be affected by the presence or absence of oxygen.

As indicated previously, it is only practicable to manage the aeration status of the soil-waste environment when the disposal operation is conducted at the soil surface (land spreading

or spray irrigation of wastes). However, the effects of anaerobic conditions should be taken into consideration in any disposal operation, particularly for wastes with a significant content of heavy metals or organics. For example, heavy metal-bearing wastewater treatment sludges formed by alkaline precipitation should not be disposed of in a municipal refuse or other organic waste environment; the organic acids formed during anaerobic decomposition would interact with the sludge, reversing the treatment procedure and freeing the heavy metals for migration.

RELATIVE ATTENUATION OF SELECTED TRACE CONTAMINANTS

A soil class or group represents a segment of a spectrum of soil properties with sufficient like characteristics as to have been separated out on the basis of practical agricultural use and genetic characteristics. In predicting how each trace contaminant may be attenuated relative to another contaminant in a soil, it must be kept in mind that within a given soil-group class, properties such as texture, clay mineral, pH value, structure and organic matter vary from place to place. As an aid in selecting the best of several soils for attenuation of contaminants, information is presented here on the chemical and physical properties and the attenuation classifications of the soils used in the study at The University of Arizona. This information can be compared to the properties of the soils in question in order to rank them according to their attenuation potential. The ranking of the soils used in The University of Arizona study is based on work with municipal landfill leachate; there is indication from the preliminary results of another EPA study* that the ranking is also valid for attenuation of trace contaminants in leachates from some industrial wastes.

* Dugway Proving Ground, "Migration of Hazardous Substances through Soil." Unpublished Progress Report prepared for the Solid and Hazardous Waste Research Division, EPA Municipal Environmental Research Laboratory, Cincinnati, Ohio. Interagency Agreement EPA-IAG-D4-0443. January 1975.

Table 3.1. CHARACTERISTICS OF THE SOILS USED IN ARIZONA SOIL-COLUMN RESEARCH

Soil Series	Soil Order	Soil Paste pH	Cation Exch. Capac. meq/100g	Elec. Cond. of Extract $\mu\text{hos/cm}$	Column Bulk Density g/cm^2	Sand Silt Clay %	Texture Class	Predominant * Clay Minerals
Magram	Ultisol	4.2	2	225	1.89	88 8 4	loamy sand	Kaolinite, chlorite
Ava	Alfisol	4.5	19	157	1.45	10 60 31	silty clay loam	Vermiculite, kaolinite
Kalkaska	Spodosol	4.7	10	237	1.53	91 4 5	sand	Chlorite, kaolinite
Davidson	Ultisol	6.2	9	169	1.89	19 20 61	clay	Kaolinite
Molokai	Oxisol	6.2	14	1262	1.44	23 25 52	clay	Kaolinite, gibbsite
Chalmers	Mollisol	6.6	26	288	1.60	7 58 35	silty clay loam	Montmorillonite, Vermiculite
Nicholson	Alfisol	6.7	37	176	1.53	3 47 29	silty clay	Vermiculite
Fanno	Alfisol	7.0	33	392	1.48	35 19 46	clay	Montmorillonite, Mica
Mohave	Aridisol	7.3	10	615	1.78	52 37 11	sandy loam	Mica, Kaolinite
Mohaveca	Aridisol	7.8	12	510	1.54	32 28 40	clay	Mica, Montmorillonite
Anthony	Entisol	7.8	6	328	2.07	71 14 15	sandy loam	Montmorillonite, Mica

* Listed in order of importance

Table 3.2. THE CATION EXCHANGE CAPACITY, EXCHANGEABLE CATIONS, SURFACE AREA, FREE IRON OXIDES, AND TOTAL Mn OF SOILS USED IN THE COLUMN RESEARCH

Soil Series	Surface Area m ²	Free Iron Oxides %	Total Mn ppm	Cation Exchange Capacity	Exchangeable Cations			
					Na	K	Ca	Mg
					-----meq/100g soil-----			
Wagram l.s. (N. Carolina)	8.0	0.6	50	2	0.20	0.40	0.60	0.60
Ava si.c.l. (Illinois)	61.5	4.0	360	19	0.43	0.23	1.33	2.63
Kalkaska s. (Michigan)	8.9	1.8	80	10	0.10	0.06	0.80	0.10
Davidson c. (N. Carolina)	51.3	17.0	4100	9	0.31	0.16	3.40	1.58
Molokai c. (Hawaii)	67.3	23.0	7400	14	0.20	0.70	6.00	4.10
Chalmers si.c.l. (Indiana)	125.3	3.1	330	26	0.20	0.10	20.60	8.60
Nicholson si.c. (Kentucky)	120.5	5.6	950	37	0.70	0.19	21.80	5.82
Fanno c. (Arizona)	122.1	3.7	280	33	0.35	0.87	17.10	7.82
Mohave s.l. (Arizona)	38.3	1.7	825	10	0.40	0.50	8.90	1.80
MohaveCa c.l. *	127.5	2.5	770	12	0.41	0.88	6.20	4.30
Anthony s.l. (Arizona)	19.8	1.8	275	6	0.15	0.38	3.85	1.23

* Free lime (CaCO₃) is present as a natural constituent.

Table 3.3. THE EXCHANGE ACIDITY, EXCHANGE CAPACITY AND CERTAIN EXCHANGEABLE ELEMENTS FOUND IN THE NEUTRAL TO ACID SOILS* USED IN THE SOIL-COLUMN RESEARCH

Soils	Exchange Acidity	Exchange Capacity	Exchangeable Element								
	meq/100 ml	meq/100 ml	Ca	Mg	N	P	K	Cu	Fe	Mn	Zn
			-----µg/ml soil-----								
Wagram	0.7	0.7	100	20	3	2.0	16	1.0	44	0.5	0.05
Ava	9.5	4.4	350	320	9	2.0	50	7.0	100	3	2.1
Kalkaska	2.7	1.1	190	20	12	17.0	34	1.0	+150	0.5	3.2
Davidson	0	5.1	690	195	3	4.0	38	2.5	16	16	0.8
Molokai	0	10.9	1400	480	35	21.0	214	13.5	14	49	7.0
Chalmers	0	28.5	3800	1140	3	1.0	36	3.0	7	3	1.0
Nicholson	0	36.5	5800	900	3	26.0	50	1.5	14	3	1.3

* Analysis provided by Hunter, Agricultural Environmental Systems, Inc., Raleigh, N.C.

Table 3.4. CONCENTRATION RANGES OF SOME COMMON CATIONS AND ANIONS OF THE SOIL-SOLUTION
DISPLACEMENTS FROM COLUMNS LEACHED WITH DEIONIZED WATER*

Soil Series	Effluent pH	Elect. Cond. µmhos/cm	K	Na	Ca	Mg	-----ppm-----			
							Cl	NH ₄	P	Si
Wagram l.s.	5.3-6.2	13-270	.6-11	T-15 ⁰	1-26	.1-1.6	.1-31	.2-.5	#	T-.6
Ava si.c.l.	4.8-5.3	24-160	1-3.2	T-8	2-5	.5-7	1-22	.06-.2	#	.6-2.8
Kalkaska s.	4.5-5.0	40-200	.5-8	T-6	2-17	.3-3	3-11	.4-2.6	#	.1-.25
Davidson c.	6.0-6.8	36-303	.5-2.4	T-4.8	3-35	1-14	1-27	.1-.2	#	.1-.2
Molokai c.	7.1-7.8	120-1500	7-20	2-107	6-105	5-58	1-320	.4-5	#	.6-1.3
Chalmers si.c.l.	7.0-7.4	37-310	T-1.1	4-12	3-37	1-12	2-17	.3-.4	#	T-8
Nicholson si.c.	6.4-7.1	30-180	.2-.6	.4-20	2-15	.2-3	1-24	.2-1.6	#	1-2
Fanno c.	7.2-7.7	170-370	1.5-5	6-21	9-39	9-39	#	#	T	T-.7
Mohave s.l.	6.7-8.0	45-850	2-15	2-79	5-170	1-22	1-28	.1-1.6	T-5	1.4-1.6
MohaveCa c.l.	7.4-7.9	85-430	1-4	3-25	15-200	1-22	2-20	.2-.3	#	.7-.9
Anthony s.l.	6.8-7.5	40-330	5-14	T-10	4-53	1-3	2-11	.1-.8	T-3.6	.7-1.3

* Data represent ranges of constituents for ~ 28 pore-space displacements

Below detectable limit

Table 3.5. PARTICLE SIZE DISTRIBUTION OF THE SOIL SAMPLES USED IN THE COLUMN RESEARCH

Series	S A N D					S I L T				CLAY
	Very Coarse 2-1mm	Coarse 1-0.5mm	Medium 0.5-0.25mm	Fine 0.25-0.1mm	Very Fine 0.1-0.05mm	50-20 μ	20-10 μ	10-5 μ	5-2 μ	
Wagram	7.48	20.70	32.06	21.81	5.84	2.00	1.37	1.59	3.31	3.84
Ava	0.53	0.56	1.25	0.82	0.67	12.80	21.69	15.71	9.63	30.63
Kalkaska	0.19	1.79	47.99	36.26	5.19	1.34	1.01	1.38	0.18	4.67
Davidson	0.71	2.38	6.52	6.02	3.39	3.32	4.83	4.08	7.43	61.32
Molokai	1.29	2.64	4.57	6.64	7.91	5.78	8.30	6.08	4.88	52.00
Chalmers	0.74	0.62	1.67	1.38	2.52	19.42	20.18	11.18	7.44	34.89
Nicholson	0.67	0.31	0.44	0.42	1.18	12.90	13.47	15.27	5.41	49.89
Fanno	8.45	4.87	2.40	9.96	9.06	5.92	4.27	3.05	5.56	46.46
Mohave	15.28	11.30	12.40	8.02	5.42	30.36	5.00	1.34	0.43	10.45
Anthony	18.05	13.71	17.68	12.93	8.92	7.41	2.69	2.20	1.37	15.04

Table 3.6. TOTAL ANALYSIS OF SOILS FOR TRACE METALS
AND FREE IRON OXIDES

Soil Series	Mn	Co	Zn	Ni	Cu	Cr	Fe Oxides
	-----µg/g-----						%
Wagram l.s.	50	*	40	80	62	*	0.6
Ava si.c.l.	360	50	77	110	80	55	4.0
Kalkaska s.	80	25	45	50	46	15	1.8
Davidson c.	4100	120	110	120	160	90	17.0
Molokai c.	7400	310	320	600	260	410	23.0
Chalmers si.c.l.	330	60	100	130	83	68	3.1
Nicholson si.c.	950	50	130	135	65	68	5.6
Fanno c.	280	45	70	100	60	38	3.7
Mohave s.l.	825	50	85	100	265	18	1.7
Mohave _{Ca} c.l.	770	50	120	120	200	40	2.5
Anthony s.l.	275	50	55	80	200	25	1.8

* Below detectable limit

Table 3.7. TEXTURAL CLASS AND CLAY MINERAL COMPOSITION OF THE CLAY (< 2 μ) SEPARATE OF SOILS USED IN THE POLLUTION ATTENUATION RESEARCH

Soil Series	Texture Class	Montmorillonite	Beidellite	Vermiculite	Chlorite	Mica	Kaolinite	Other
Wagram	Loamy sand	0	0	0	3*	1	4	Quartz-3
Ava	Silty clay loam	2 [@]	0	3	0	2	3	Quartz-2
Kalkaska	Sand	0	0	0	3*	1	2	Quartz-2
Davidson	Clay	0	0	0	1	0	5	Gibbsite-1
Molokai	Clay	0	0	0	0	2	4	Gibbsite-3
Chalmers	Silty clay loam	4	0	2	2	0	2	Quartz-2
Nicholson	Silty clay	0	0	5	0	1	1	Quartz-2
Fanno	Clay	3	0	0	0	2	1	Quartz-2
Mohave	Sandy loam	2	0	0	0	4	3	Quartz-2
MohaveCa	Clay loam	3	0	0	0	4	2	Quartz-2
Anthony	Sandy loam	4	0	1	1	3	2	Quartz-2

* Chloritic intergrade

[@] The amount of each mineral present is represented as: predominant 5, large 4, moderate 3, small 2, trace 1, and looked-for but not detected 0.

Chemical and physical characteristics of the soils used in the Arizona study are presented in Tables 3.1 - 3.7. The soil orders represented are shown in Table 3.8 below.

TABLE 3.8. THE SOIL ORDERS REPRESENTED IN THE ARIZONA STUDY

Soil Order	Great Soil Group description	Series name	State location
Ultisol	Red Yellow Lateritic	Wagram	N. Carolina
Alfisol	Gray Brown Podzolic	Ava	Illinois
Spodosol	Podzol	Kalkaska	Michigan
Ultisol	Red Brown Lateritic	Davidson	N. Carolina
Oxisol	Red Lateritic	Molokai	Hawaii
Mollisol	Prairie	Chalmers	Indiana
Alfisol	Gray Brown Podzolic	Nicholson	Kentucky
Alfisol	Reddish Brown	Fanno	Arizona
Aridisol	Red Desert	Mohave	Arizona
Aridisol	Red Desert/lime	Mohave (Ca)	Arizona
Entisol	Alluvial	Anthony	Arizona

Attenuation Comparisons Between Soils

One of the most critical factors affecting attenuation is particle-size distribution. For example, Anthony which has the same dominant clay mineral, montmorillonite, as Fanno, attenuated the trace contaminants As, Be, Cd, Cr, Cu, Fe, Pb, Hg, Se and Zn to the least extent of all soils (except Wagram which is even coarser textured), and Fanno, most often, appeared at the top of the list for attenuation. Anthony is classed as a sandy loam, and Fanno as a clay. See Tables 3.5 and 3.7 for information on the texture and

clay mineralogy of the soils. Wagram, a loamy sand whose clay mineralogy is dominated by kaolinite, and kalkaska, a sand that contains a small amount of kaolinite but is dominated moderately by chlorite, attenuate the trace elements somewhat similarly and to an extent only slightly better than Anthony and much poorer than Davidson, a clay dominated by kaolinite.

The ion exchange capacity appears to be less well correlated with trace element retention than other soil parameters as colloid and "free" iron oxide. Those soils highest in cation exchange capacity (CEC), however, also were those which contained more clay and retained the most trace contaminants. Additional study must be conducted before CEC can be said to relate directly to attenuation of the selected trace elements.

The nature of the soil colloid fraction (i.e., that measured as $< 2\mu$ clay) appears to have a highly significant effect on attenuation. There is some evidence in our preliminary studies that Molokai, which is high in hydrous oxides and oxides of Fe (the clay is kaolinitic-like) also is unusually active in attenuation. It contains only slightly more colloid than Fanno and Nicholson, but less than Davidson.

The only soil that contained appreciable quantities of organic matter was Kalkaska, a Spodosol. It is so very sandy that leachates contained infiltrated organic matter and therefore the effect of organic matter could not be evaluated readily.

Thus, the major properties which appeared to influence attenuation for the soils studied are: (a) texture, (b) iron oxides, (c) content of the $< 2\mu$ colloid, (d) lime, and (e) pH value.

Lime effects are being studied with two soils (one containing natural lime and one without lime) of the same series, Mohave. Early data lead to the belief that the effect of natural lime in soil is an important factor in attenuation since the pore space displacements of leachate from lime Mohave are freer of the trace metals than those of lime-free Mohave. Furthermore, research involving the use of a 2-cm layer of ground Kentucky agricultural

Table 3.9. RELATIONSHIP BETWEEN CERTAIN MEASUREABLE PARAMETERS OF 11 REPRESENTATIVE SOILS AND ATTENUATION OF SELECTED TRACE CONTAMINANTS OF LANDFILL LEACHATES

Soil Series	Soil pH	Colloid <2 μ (clay) %	Silt	Cation Exchange Capacity meq/100g	Mineral Nature of Colloid	"Free" Iron Oxide %	Attenuation Class*
Davidson	6.2	61	20	9	Kaolinite	17.0	2
Molokai	6.2	52	25	14	Kaolinite (Fe ₂ O ₃)	23.0	1
Nicholson	6.7	49	47	37	Vermiculite	5.6	1
Fanno	7.0	46	19	33	Montmorillonite	3.7	2
MohaveCa	7.8	40	28	12	Mica	2.5	3
Chalmers	6.6	35	52	26	Montmorillonite	3.1	3
Ava	4.5	31	60	19	Kaolinite	4.0	3
Anthony	7.8	15	14	6	Montmorillonite	1.8	5
Mohave	7.3	11	37	10	Mica	1.7	4
Kalkaska	4.7	5	4	10	Chlorite	1.8	5
Wagram	4.2	4	8	2	Chlorite	0.6	5

* Rough estimate for all trace contaminants (1 is high attenuation, 5 is low).

limestone over a 10-cm soil layer greatly reduced the migration of several trace elements through the soil columns.

The soils representing seven major soil orders are listed in Table 3.9 in a decreasing order of percentage of soil colloid to allow comparison on the basis of some of the soil factors affecting attenuation. According to data listed, the proportion of silt and clay in soils is quite variable. Ava, for example, assumes sixth position (31%) from the top in colloid, but first (60%) in silt. Nicholson, which is one of the best attenuator soils, ranks third in colloid and second in silt. It contains very little sand ($\sim 4\%$). Silt also exerts important adsorption properties and must not be overlooked as contributing substantially to attenuation of trace metals.

The last column in Table 3.9 is an attempt to broadly evaluate the soils according to their attenuation characteristics of the trace contaminants considered in this manuscript. To further evaluate the soils for attenuation characteristics of individual trace elements "spiked" into landfill leachate, Table 3.10 is presented which gives the pore-volume in which the element first appeared in the soil-column effluent. The obvious conclusion is that texture is a critical factor in attenuation in soils; perhaps the most important. Because of its wide variation among soils, even within the same order, texture always will play a leading position in attenuation of trace contaminants.

Soil structure may also be important since it, too, like texture, relates to pore-size distribution and available surfaces for chemical and physical reactions. Because of structure, soil surface area does not relate exactly with the clay content, although in a broader comparison as the soil particles become smaller, the soil surface area increases. Compare the last two columns in Table 3.11. Soil structure is almost impossible to describe. Even in soils taken into the lab, after carefully sampling in what often is termed "undisturbed conditions," the structure is altered as compared with its natural state in the field.

TABLE 3.10. THE PORE VOLUME IN WHICH THE ELEMENT FIRST APPEARED IN THE SOIL-COLUMN EFFLUENT

Soil		As	Be	Cd	Cr	Cu	Pb	Se	Zn	Hg
Series	pH									
Wagram	4.2	1	1	1	1	20*	1	4	1	1
Ava	4.5	5	3	1	7	10	10	21*	1	1
Kalkaska	4.7	1	4	2	1	19*	17*	10	1	1
Davidson	6.2	13*	6	3	17*	27*	26*	17*	5	1
Molokai	6.2	13*	12*	30	19*	13*	22*	14*	27*	7
Nicholson	6.7	12	5*	13	5	12*	16*	8*	7	1
Fanno	7.0	1	4*	14*	1	15*	16	3*	13*	4
Mohave	7.3	1	13	13	1	19*	16*	2	17	5
Mohave _{Ca}	7.8	10*	6*	8	1	15*	23*	6	11*	6
Anthony	7.8	1	5	2	1	15	17	2	2	1

*None of the elements appeared in the effluent for the listed number of pore volumes.

TABLE 3.11. THE pH VALUE, CLAY AND SURFACE AREA OF SOILS USED IN THE COLUMN RESEARCH

Soil Series	pH	< 2 μ Clay	Soil surface area
		%	cm ² /g
Wagram loamy sand	4.2	4	8
Ava silty clay loam	4.5	31	62
Kalkaska sand	4.7	5	9
Davidson clay	6.2	61	51
Molokai clay	6.2	52	67
Chalmers silty clay loam	6.6	35	126
Nicholson silty clay	6.7	49	121
Fanno clay	7.0	46	122
Mohave sandy loam	7.3	11	38
Mohave _{Ca} clay loam	7.8	40	128
Anthony sandy loam	7.8	15	20

Because certain soil orders, such as Spodosol, are very sandy, they usually are poor attenuators of trace contaminants compared with other soils. Oxisols, on the other hand, tend to be good attenuators since they are characteristically fine textured, contain a high amount of hydrous oxides, and are deep. Entisol (alluvial) is one order that is quite variable in texture. It represents a dominant position in landfill sites since alluvial soils occur on low river terraces, river bottoms, coarse-textured alluvial fans, gravel pits, and often represent the least economic land. Entisols also may represent highly productive (agriculturally) soils bordering large streams and rivers and pocketed along small water channels.

In conclusion, it is encouraging that certain readily measurable soil parameters "stand out" as critical factors affecting attenuation and broad predictions may be drawn with some confidence at an early date with respect to soil attenuation of trace contaminants. It is important that the research proceed further, comparing soils having similar textures (and soil surface areas) but dissimilar clay minerals, pH, lime, cation exchange capacity, soluble salt and hydrous oxides in an orderly and variably controlled fashion, if the most effective disposal control practices are to evolve and we are to acquire sufficient evidence to establish the best practices for waste disposal on land.

SECTION IV

SOILS AND GEOLOGICAL MATERIAL

This discussion on soils and geological materials is presented as background for understanding the processes which affect the migration rate of metals in soil. Additionally, it is hoped that the reader will gain some appreciation of the complexity of the soil environment and of the consequent difficulty of obtaining simple, general solutions for the problems involved in land disposal of wastes.

THE SOIL

The soil is a complex, dynamic biological, chemical, and physical system which transforms all matter, including waste materials. Some components of the wastes are permanently incorporated into the system while others pass through and eventually enter underground water or are expelled into the air as gases. It is necessary to become acquainted with the major components of soils which are involved in the transformations of wastes to understand why soils attenuate. Waste components and a soil's effectiveness in functioning as an attenuator are related to its physical, chemical, and biological properties.

Major Components

Soils contain inorganic and organic solids, water, air, and microorganisms. Generally, the soil scientist thinks of a good agricultural or garden soil as being medium textured (silt loam) consisting of about 45 percent mineral matter, 5 percent organic matter, and 50 percent pore space of which half is filled with water and half with air.

Organic Solids--

Organic solids constitute the bulk of organic matter in soils. Organic matter originates in part from plant constituents resistant to decay, such as degraded lignin, waxes, and resins, and in part from living and dead microorganisms, synthesized microbial gums and slimes, and other microbial cell debris. Organic matter concentrates almost wholly in the surface layer of soils. Landfills are characteristically excavated into subsoil material which is low in organic matter. The discussion in this manuscript, therefore, will deemphasize the soil organic fraction. Interactions of the hazardous constituents with degraded and synthesized organic constituents contained in leachates from municipal refuse, however, will be included. The biochemical route that decay takes is about the same, but the rate may vary from soil to soil. For example, under aerobic conditions paper will decay primarily into gas and water and leave about the same kind and amount of residue regardless of the soil in which it is placed.

Inorganic Solids--

The characteristics of inorganic solids in soil vary considerably, and each soil has a nearly unique set of properties. One of the important physical properties of soil inorganic solids is the distribution of particle sizes between sand (2.00-0.02 mm diameter), silt (0.02-0.002 mm), and clay (0.002 mm). The textural classification of a soil is based on the percentage of different sizes of particles it contains (Figure 4.1). See Appendix B for additional information on particle size and texture in the USDA and USCS systems. Sand and silt particles are composed mostly of quartz and primary silicate minerals which are relatively insoluble and complex in structure and composition. The types and amounts of primary minerals in soil are governed by the mineral composition of the parent material from which the soil originated. The clay-sized and colloidal materials are composed mostly of secondary materials (Figure 4.2), which are weathering products of primary minerals. The types of secondary minerals in a soil are governed not only by the primary minerals but also by the weathering conditions and the rate of removal of the weathering products (Figure 4.3).

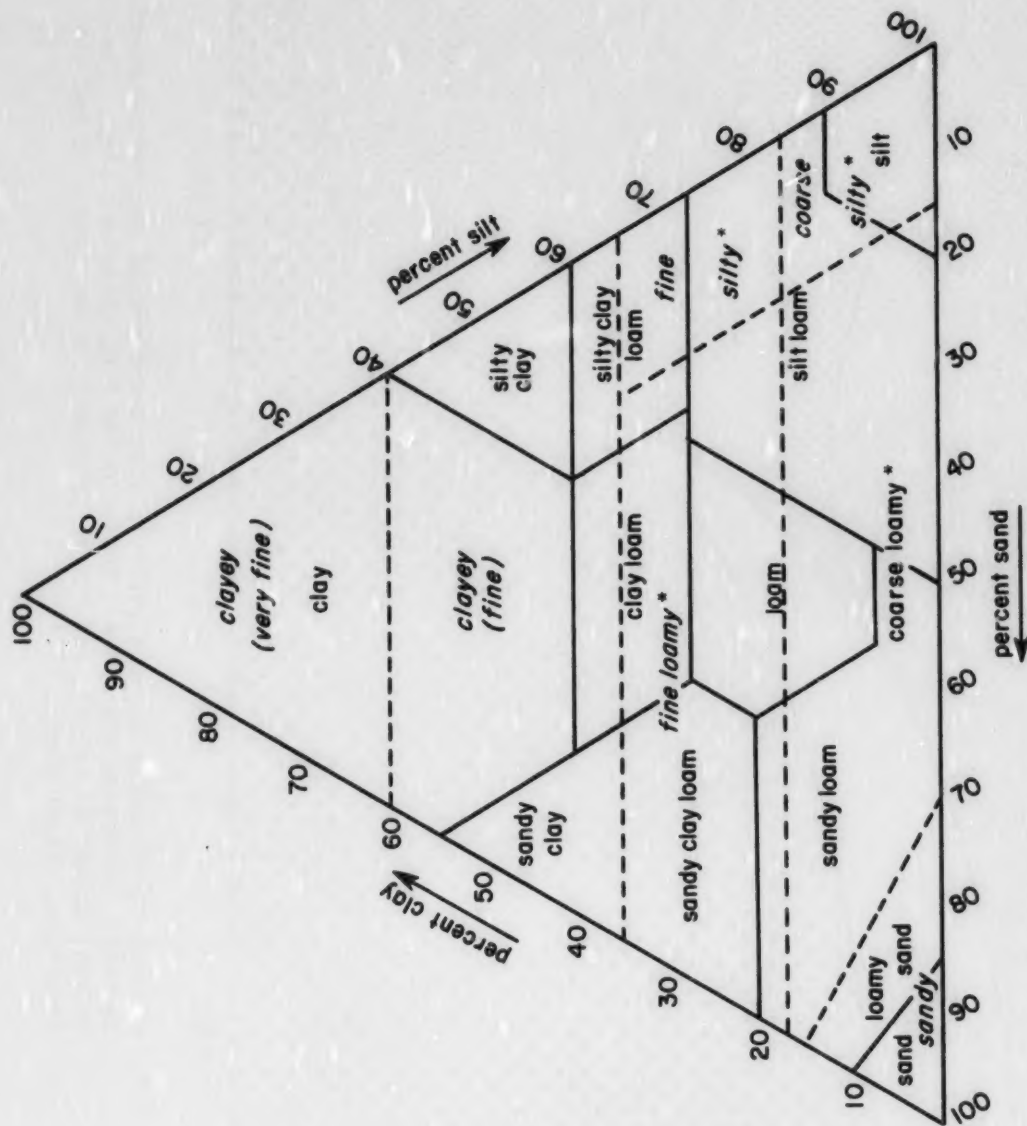


Figure 4.1. Textural classification (USDA) of soil based on the percentage of different sizes of particles it contains.

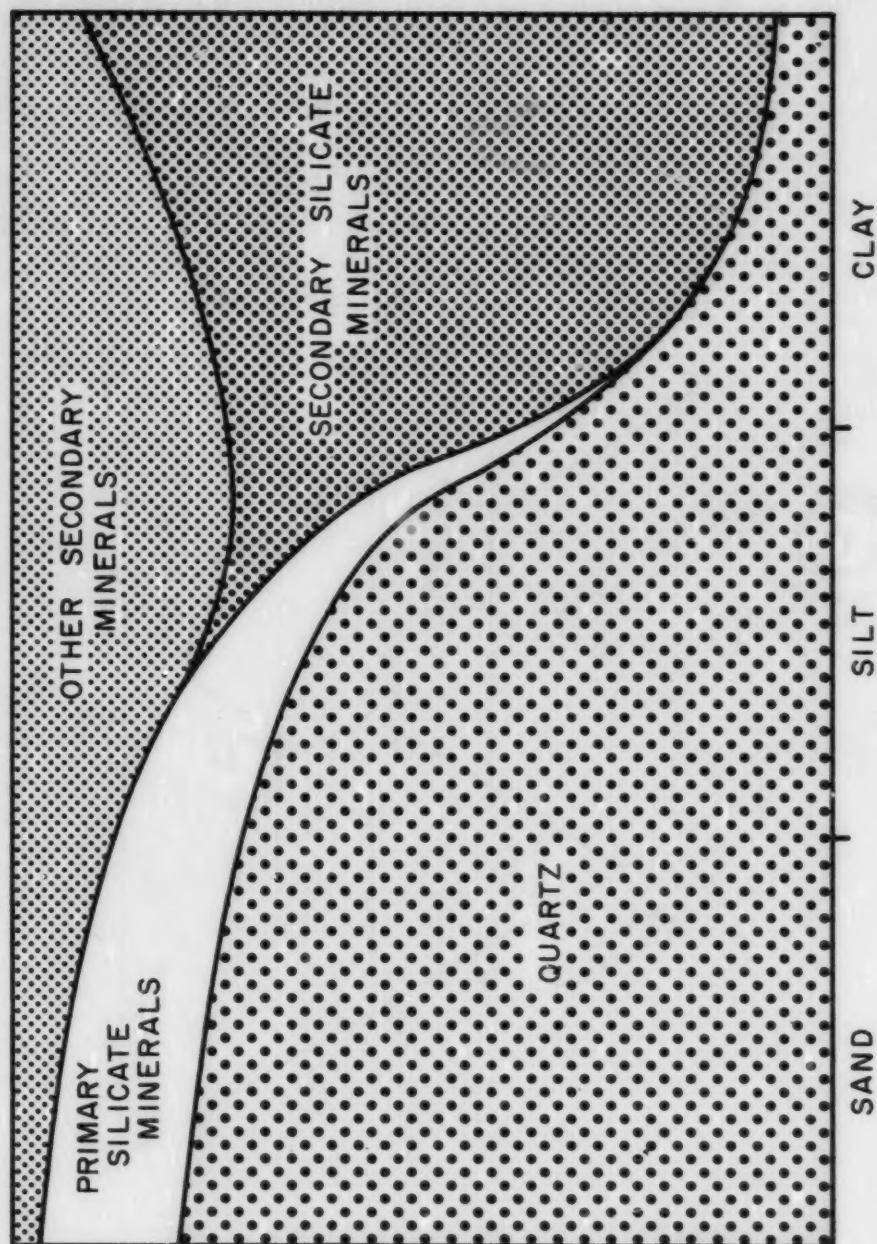


Figure 4.2. General relationship between particle size and kinds of minerals present. Secondary silicates (Fe and Al) dominate the fine colloidal clay. The Hydrous oxides of Fe, Al, and Mn are prominent in the fine silt and clay fractions. (From Brady, 1974)

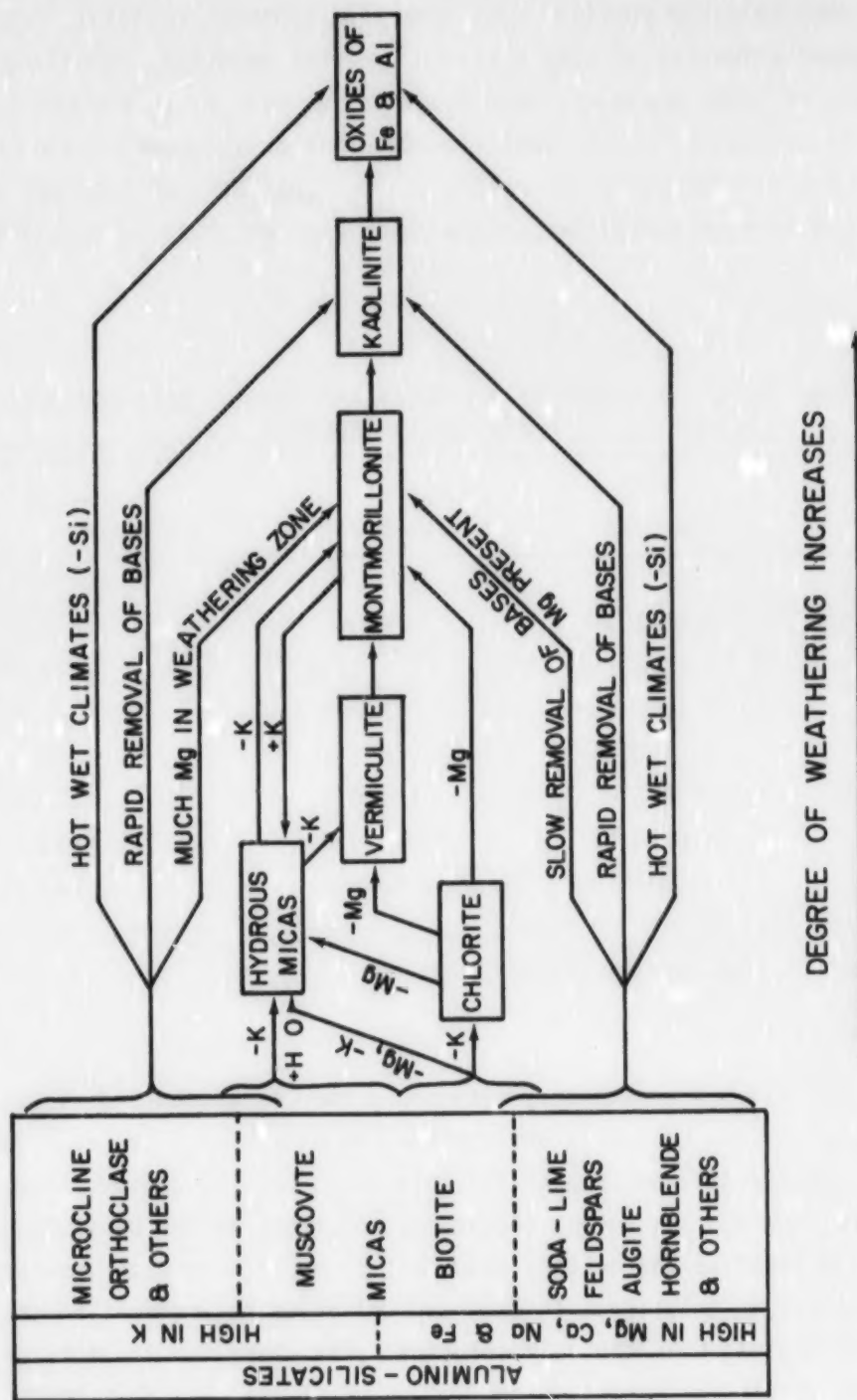


Figure 4.3. General conditions for the formation of the various silicate clays and oxides of iron and aluminum. Clay genesis is accompanied by the removal of solubilized elements such as K, Na, Ca, and Mg. (From Brady, 1974.)

The colloidal fraction of the soil controls the majority of biological, chemical, and physical reactions. In subsoils colloidal fraction is composed primarily of clay although the very reactive oxides and hydrous-oxides of iron, manganese, and aluminum, as well as some organic matter, may be present in significant amounts. Not only is the surface area (Table 4.1) of colloidal particles vastly greater than that of sand and silt, but the surface carries a negative charge which attracts cations (metallic elements).

TABLE 4.1. COMPARISONS IN NUMBER OF PARTICLES AND SURFACE AREA PER UNIT WEIGHT FOR DIFFERENT SOIL SEPARATES

Texture* (Particle size)	Diameter	Number	Surface area
	mm	g	g/cm ²
Fine gravel	2.00-1.00	90	11.3
Coarse sand	1.00-0.50	722	22.7
Medium sand	0.50-0.25	5,777	45.4
Fine sand	0.25-0.10	46,213	90.7
Very fine sand	0.10-0.05	722,074	226.9
Silt	0.05-0.002	5,776,674	453.7
Clay	below 0.002	90,260,853,860	11,342.5

* U.S Department of Agriculture classification

The soil clays are secondary minerals formed by weathering of geological material. They basically are composed of aluminum silicates. Table 4.2 compares the relative amounts of silicate clays and the hydrous oxides in soils as related to climate and geographic locations in the USA. Because clays possess a negative charge they hold cations subject to later exchange with other cations in solution. In this way, elements become delayed in their downward migration in the soil solution. The charge on the surface of some clay-size particles changes, depending on pH of the soil as a whole.

TABLE 4.2. DOMINANT CLAY MINERALS FOUND IN DIFFERENT SOIL ORDERS OF THE COMPREHENSIVE CLASSIFICATION SYSTEM*

Soil order	General Weathering Intensity		Typical location in USA	Hydrous oxides		Montmorillonite		Illite		Vermiculite		Inter-Chlorite grades
	Low	High										
Entisol			Variable			X		X				
Inceptisol			Variable					X				X
Aridisols			Desert					X		X		X
Vertisols			Ala, Tex Central USA			X						
Mollisols						X		X		X		X
Alfisols			Ohio, Pa, N.Y.		X	X		X		X		X
Spodosols			New England SE USA	X				X				X
Ultisols				X						X		X
Oxisols	High		Tropical zones	X		X						X

* Adapted from Jackson (3).

Table 4.3 shows some of the striking differences in the chemical and physical properties of the three major clay minerals.

TABLE 4.3. COMPARATIVE PROPERTIES OF THREE MAJOR TYPES OF COLLOIDS*

Property	Type of Colloid		
	Montmorillonite	Illite	Kaolinite
Size (microns)	0.01 - 1.0	0.1 - 2.0	0.1 - 5.0
Shape	irregular flakes	irregular flakes	hexagonal crystals
External surface	high	medium	low
Internal surface	very high	medium	none
Cohesion, plasticity	high	medium	low
Swelling capacity	high	medium	low
Cation exchange capacity (*me/100 gm)	80-100	15-40	3-15

* From Buckman and Brady (1960)

Aluminum and iron hydroxide gels, oxides, and mixed hydroxide/oxide compounds act strongly to absorb, combine with, and precipitate hazardous substances and elements. The hydrous manganese oxides also should be included in this group. This is a group of soil chemicals which coat as well as form particles and are dominant in numerous attenuation mechanisms.

Soil Water--

The vehicle in which most constituents are transported through soils is water. The movement of water is a continual, naturally occurring process governed by potential gradients originating from water addition, gravity, capillary action, evaporation, temperature differences, variable salt concentration, matrix deformation, and plant extraction. The mechanism operating during the redistribution of water and solutes in soils and reliable methods for assessing hydraulic properties of field soils must be defined before transfer processes can be accurately predicted.

The movement of water in soil takes place through the pore spaces. The rate of flow is controlled by the size and distribution of the pore spaces and the total pore volume. Such gross physical characteristics as texture (particle size distribution), structure (arrangement of the particles into crumb-like, blocky, etc., units; see Figure 4.4 below), bulk density (compaction), swelling and shrinking, wettability, and pore clogging, affect water movement. Structure can have a pronounced effect on water flow patterns and migration of pollutants. The spaces between structural units can provide pathways for liquid movement so that solutions passing through the soil may come into contact with only a small proportion of the soil material, giving pollutants in solution less opportunity to be attenuated.

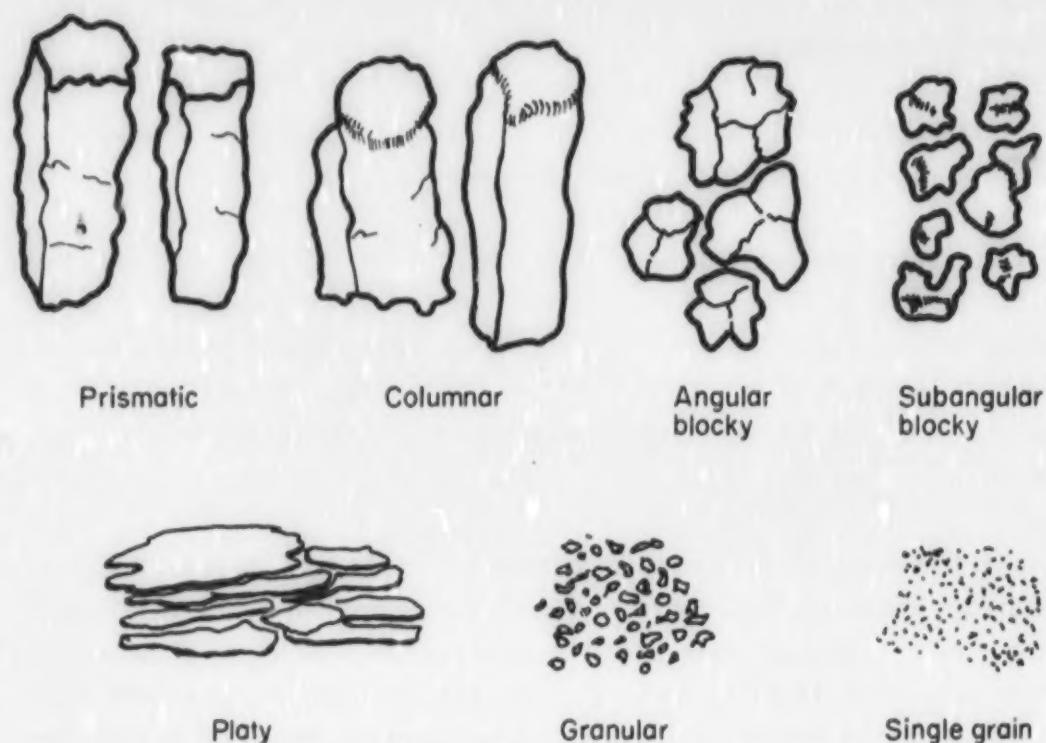


Figure 4.4. Classification of soil structures (From Fuller, 1974).

The water flow or flux through a soil is an important factor in attenuation and movement of potentially hazardous pollutants. If water does not flow, migration of pollutants virtually stops. Attenuation reactions proceed at some finite rate and for the same amount of solution passed through soil, the greater amount of attenuation would be associated with the slower flow rate because sufficient time would be available for attenuation mechanisms to be fully effective.

Soil Air--

Composition of the soil air differs appreciably from that above the soil surface because of microbial and chemical activity taking place within the soil. Carbon dioxide and nitrogen are higher, and under reducing conditions (as would be expected below disposal sites), gases such as hydrogen sulfide, methane, and some of the oxides of nitrogen may be present in significant concentrations.

Generation of any gas within the soil inhibits the flow of water through the soil by blocking the soil pore spaces.

Evolution of carbon dioxide is particularly significant because of the role it plays in pH (Figure 4.5). As the carbon dioxide dissolves in water it forms carbonic acid and buffers the soil solution at a pH below 6.0. A lowered pH increases the solubility of pollutants from the solid phase of a waste and increases the mobility of hazardous materials once they are in solution.

Presumably, if the hazardous materials are present in solution in high enough concentration, they can sterilize the soil at least in the near vicinity of the disposal site, greatly reducing the production of gases. Farther away from the site, because of dilution or other physical and chemical attenuation processes, concentrations are lowered enough to permit biological activity and production of gases. Even if microbial activity is inhibited because of toxic materials in solution, carbon dioxide can still be formed because of the reaction between leachates from an inherently acidic waste and carbonates (free lime) present in the soil.

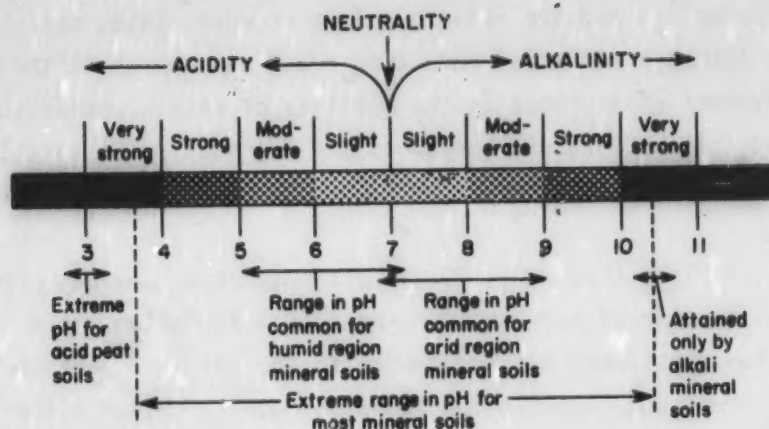


Figure 4.5. Classification of soil pH range.

Soil Microorganisms--

Soils are abundantly supplied with microorganisms capable of decomposing all organic substances. Although such microbially resistant materials as rubber, plastics, and waxes decay very slowly, they do decay. Even metals and metallic compounds are transformed (oxidized or reduced) by microorganisms. The majority of organic materials (paper, grass clippings, food scraps, etc.) decay relatively rapidly. If this were not so, the earth's surface would be literally a huge garbage pile, and life would long since have been smothered in its own debris.

Microbial degradation of waste and debris is a continual process. The transformation of wastes takes place most rapidly when they are mixed with the soil and more slowly when they lie on top of it or layered in it. Under conditions of plentiful oxygen, the mineral constituents are oxidized and most become relatively immobile, although those that form soluble organic complexes or chelates are protected, at least for awhile, from further oxidation and are thus free to migrate. When microbial processes consume oxygen faster than it can diffuse into the soil, anaerobic conditions develop followed by reducing conditions as substances other than oxygen are

used as electron acceptors and are reduced. In a reduced state, most metals are more mobile. Although oxidation-reduction reactions represent the most significant involvement of microbes in the mobility of metals, other involvements such as production of organic compounds and degradation of soluble metal-organic complexes are important.

The microbial flora (bacteria, fungi, actinomycetes, amoeba, protozoa, algae, and others) capable of carrying out these transformations (i.e., oxidation and reduction reactions) are indigenous to the soil and present in great abundance. Seeding or inoculation is not needed to change either the rate or route of biochemical change.

SOIL CLASSIFICATION AND ATTENUATION

This section gives a brief description of the U.S. Department of Agriculture (USDA) system of classifying soils and of some of the soil characteristics used in classification. By knowing certain characteristics of soils, general predictions can be made concerning trace and heavy metal reactions. These predictions are assumed to be valid wherever these soils occur, i.e., are identified and mapped in the United States. Data on attenuation properties of certain classifications of soils are presented in Section V.

It is unrealistic to expect any element to react or move the same in a soil developed in Michigan as one developed in Florida. Soils are a product of both their environment and their parent material and since both differ from one location to another, soil characteristics also differ, particularly in their attenuation properties. To elaborate, soils developed under the same high rainfall conditions in Michigan or Florida, and from the same parent rock may be quite different. In Michigan, a Spodosol (Podzol) may form; in Florida, an Oxisol (Laterite) may develop. The Spodosol is found in temperate to cold climates, the oxisol in subtropical to tropical climates. The two soils do not attenuate trace and heavy metals in a similar way. Laboratory data from the study at The University of Arizona

indicate that the spodic soil allows far greater migration to take place than does the oxic soil.

The USDA tentatively recognizes the 10 orders listed in Table 4.4.

TABLE 4.4. PRESENT SOIL ORDERS AND APPROXIMATE EQUIVALENTS IN REVISED CLASSIFICATION

Present Order*	Approximate equivalents #
1. Entisols	Azonal soils, and some Low Humic Gley soils.
2. Vertisols	Grumusols.
3. Inceptisols	Ando, Sol Brun Acide, some Brown Forest, Low-Humic Gley, and Humic Gley soils.
4. Aridisols	Desert, Reddish Desert, Sierozem, Solonchak, some Brown and Reddish Brown soils, and associated Solonetz.
5. Mollisols	Chestnut, Chernozem, Brunizem (Prairie), Rendzinas, some Brown, Brown Forest, and associated Solonetz and Humic Gley soils.
6. Spodosol	Podzols, Brown Podzolic soils, and Ground-water Podzols.
7. Alfisols	Gray-Brown Podzolic, Gray Wooded soils, Noncalcic Brown soils, Degraded Chernozem, and associated Planosols and some Half-bog soils.
8. Ultisols	Red-yellow Podzolic soils, Reddish-brown Lateritic soils of the U.S., and associated Planosols and Half-bog soils.
9. Oxisols	Laterite soils, Latosols.
10. Histosols	Bog soils.

* Present (1960, 1968) USDA comprehensive soil classification

Old (1938) USDA soil classification

In the studies at The University of Arizona, the following orders are represented, Entisol, Aridisol, Mollisol, Spodosol, Alfisols, Ultisol, and Oxisol. Vertisol and Histosol were not included because they represent only limited acreages of suitable potential site locations as compared to the other soils. Because of the widespread distribution of Alfisols in the United States and

certain differences in soil characteristics which are expected to critically influence attenuation, three Alfisols of quite different climatic location and chemical and physical parameters were selected for research.

In the present USDA comprehensive soil classification there are 10 orders, the highest category in the classification. These are further subdivided into 43 suborders and approximately 200 Great Groups. Successively lower and more numerous categories of the classification are Subgroups, Families, and Series. Although the Orders contain soils with similar properties, in some the chemical and physical properties affecting attenuation may vary as much for soils within the same Order as for soils in different orders. Nevertheless, the groupings in the classification are of use in predicting ion mobility because many of the classification criteria are soil properties which affect attenuation.

The USDA Soil Conservation Service (1968) points out that the lowest categories in the system, the family and series, serve purposes that are largely pragmatic: the series names are abstract and the technical family names are descriptive. The factors used to distinguish families of mineral soils within a subgroup are listed to illustrate how family differences can relate to attenuation characteristics. The justification for their presentation becomes evident after reviewing them; they could significantly influence movement of trace and heavy metals.

Particle-size classes

Mineralogy classes

Calcareous and reaction (pH) classes

Soil temperature classes

Classes of cracks

Soil depth classes

Soil slope classes

Soil consistency classes

Classes of coatings
(on sands)

Even when attenuation properties correlate well with one of the groupings in the classification system, man may so alter the soil environment

by his activities that the soil classification, in the volume of soil affected, is no longer useful as a guide for selecting a waste-disposal site. For example, the accumulation of leachate in soil below a municipal landfill may change the environment from aerobic to anaerobic and strongly reducing, thereby promoting the solubility and movement of metals. If the depth of soil thus affected includes a water-bearing formation, the disposal site can contaminate potable water supplies. On the other hand, if there is a sufficient depth of soil beneath the site, a partially aerobic, oxidizing zone may remain above the water-bearing formation and the soil classification can have significance as regards attenuation. This sort of possibility must be considered when using soil classification as a factor in site selection.

The following are descriptions of characteristics of soils in the 10 orders, the highest and most general category in the classification. These descriptions are adapted from information provided by the USDA Soil Conservation Service. See Figure B-2(A) and B-2(B) in Appendix B for a map of the geographic distribution of Orders and Suborders in the United States.

Alfisols

Alfisols have a clayey subsoil horizon and moderate to high base (cation) saturation. Water is held above the wilting point during at least three of the warm months of the year. Alfisols are higher in hydroxy-oxides (sesquioxides) than most soils, as the name implies, and therefore may have a fragipan, duripan, sodium horizon, petrocalcic (lime), and plinthite (iron oxides or sesquioxides) or other similar features which separate them from other soils. Where the temperature is moderate to cool, alfisols form a belt between the Mollisols of the grasslands, and Spodosols and Inceptisols of very humid climates. In warmer climates, Alfisols form a belt between Aridisols of arid regions and Inceptisols, Ultisols, and Oxisols of warmer climates. Leaching of bases from the soil may occur almost every year or may be infrequent.

Aridisols

Aridisols occur in arid climates. They do not have water available to mesophytic plants for long periods as do the Alfisols. Water is held at less than 15 bars or it is salty. A few Aridisols occur in semiarid climates because they take up water slowly and most of the rainfall runs off.

Aridisols have one or more pedogenic horizons that may have formed in the present dry environment or that may be relics of a former pluvial period. The pedogenic horizon may be the result of translocation and accumulation of salts, lime, or silicate clays or of cementation by carbonates or silica. The pH usually is neutral to alkaline, sometimes highly alkaline.

Entisols

Entisols do not have horizon or profile development, or at least no evidence of such. In many of the soils time has been too short for distinct horizons to differentiate. Other Entisols are on soil slopes too steep for water to penetrate well or where erosion rate exceeds development rate, still others are on flood or glacial outwash plains which continuously accumulate new alluvium. Some are windmoving sand. Not all Entisols are young. Some are actually very old, consisting mostly of quartz sand which weathers very slowly. Such materials as organic matter, lime, gypsum, iron oxides, and clays do not accumulate or at least only to a very small extent.

Histosols

Most Histosols are saturated or nearly saturated with water most of the year. They are high in organic matter and represent what is often described as mucks, peat bogs, high moors, or raised peats. For obvious reasons these soils are not included with those we are testing. Few disposal sites are located in such unstable swamps.

Inceptisols

By USDA definition (1968), in part at least, "Inceptisols are soils of humid regions that have altered horizons which have lost bases or iron and aluminum but retain some weatherable minerals. They do not have an illuvial horizon enriched either with silicate clay that contains aluminum or with an amorphous mixture of aluminum and organic matter." This is a difficult soil order to visualize from the description. It represents more what other soils are not than what they are. Inceptisols develop mainly in the more clayey parent materials, in contrast to Spodosols, which develop in materials which have little clay. No Inceptisols are included in the soils being studied at Arizona.

Mollisols

Very dark colored soils, rich in bases and naturally covered by grass (steppe land) are called Mollisols. Many soils of this order accumulate lime and/or sodium, and clay. Mollisols occupy extensive subhumid to semi-arid areas of the grass plains in the USA. They are located generally between the Aridisols of arid climates and the Spodosols or Alfisols of humid climates. These soils are highly productive, constituting rich crop land in the breadbasket areas of central and west central U.S. Areas of Mollisols appear in nearly every state. Luxuriant, perennial grass seems to be essential to their formation. Where waste waters and leachates are spread on the surface, the high soil organic matter plays an important part in mobility of trace and heavy elements. Where leachates and aqueous wastes pass through subsoils only, lime and bases influence mobility in addition to that of clay minerals.

Oxisols

Those soils which once were called red and yellow laterites are now named Oxisols. Reddish, yellowish, or grayish soils of tropical and subtropical climates that form on mostly gentle slopes on surfaces of great age are Oxisols. They are mixtures of quartz, kaolin, free oxides and

organic matter. The boundaries of horizons blend into each other so gradually they are generally arbitrary. Weathering has proceeded to great depths. Water moves through these soils rapidly. Because of the high oxide (primarily iron) content that coats particles and forms granular particulates, these soils attenuate the trace and heavy metals very well. Oxisols occur in Hawaii.

Spodosols

Two well defined and obvious-to-the-eye horizons distinguish Spodosols. Just below the surface layer of forest litter and partly decomposed dark organic matter is a bleached layer of uncoated quartz sand. The second layer, just below, usually is coffee color. Organic matter and iron complexes accumulate to give the dark brown color. However, this spodic is one in which amorphous mixtures of organic matter and aluminum may also occur with or without iron.

Spodosols generally are coarse textured, contain only small quantities of clay, if any, and usually permit rapid water movement. These soils occur under high rainfall conditions and coniferous forest, though sometimes hardwoods are present. Attenuation is poor despite the spodic horizon where aluminum, and often iron, complexes with organic matter. Usually the iron and aluminum content is low, though, even when a fragipan (soft when wet, brittle when dry) is present. The textures are mostly sandy, sandy-skeletal, coarse loam, loamy-skeletal, and coarse-silty. New England, New York, Northern lake states, and Alaska are most noted for spodic (Podzolic) soils.

Ultisols

The concept of Ultisols is that of soils of mid-to-low latitudes that have a horizon that contains an appreciable amount of translocated silicate clay but few bases. Highly humid conditions sometime during the year causes water to move through them. Ultisols are most commonly found in warm-humid climates that have a seasonal deficit of rain and on older

surfaces. They develop on a wide variety of parent materials. Kaolin, gibbsite, and aluminum-interlaid clays are common in the soil clay fraction. They usually form under coniferous and hardwood-forest vegetation in the United States.

Vertisols

Vertisols are clayey soils which crack severely when dry and have high bulk densities between the cracks. The clay minerals are dominated by montmorillonite. Most are found under warm climatic conditions, i.e., thermic or warmer. In arid regions they form in closed depressions or playas. Vertisols often are referred to as churning soils because during swelling, pressure is exerted, causing them to heave and recycle the soil. Vertisols are not included in the Arizona study. They generally do not represent suitable sites for disposals and are seldom used for this purpose.

NATURAL CONTENT OF ELEMENTS IN SOIL

The natural content of certain elements in soil is of importance because this is the "background" against which the degree of soil contamination by waste disposal must be judged. Additionally, under certain conditions, many of the naturally occurring trace and heavy elements in soils may be solubilized and contribute significantly to pollution of surface and groundwaters. Hence, a summary of some information on this subject is presented here.

Arsenic

An average content of arsenic in soils is estimated by Cavender (1964) and Vinogradov (1959) as being about 5 ppm. Soils contain between 1 and 10 ppm arsenic unless contaminated, according to Warren et al. (1964). Ash of plant material is much higher in arsenic than soils. For example, Goldschmidt (1964) reports up to 320 ppm As in the ash from the uppermost humus layer of a beech forest. There appears to be an arsenic-sulfide relationship in lower soil horizons above sulfide-rich parent materials.

According to Presant and Tupper (1966), who studied 21 Spodic (Podzol) soil profiles, the mean values of total arsenic ranged from 2 ppm in the surface A₀ horizons above nonmineralized bedrock to 1,100 ppm in the C horizon of profiles over sulfide deposits (Table 4.5). See Tables 4.6 and 4.7 for As contents of a large number of soil and rock samples, and Table 4.8 for a comparison of the concentration of trace metals in igneous and sedimentary rocks, seawater, and soils.

TABLE 4.5. MEAN CONTENTS AND RANGES OF ARSENIC IN WELL DRAINED NEW BRUNSWICK PODZOL PROFILES*

No. of Profiles sampled	Above "normal" bedrock		Above sulfide deposits	
	-- + 13		-- + 7	
	Mean As ppm	Range ppm	Mean As ppm	Range ppm
A ₀ horizon	2	0-10	530	70-1100
A ₂ horizon	5	0-40	620	0-1900
B ₁ horizon	22	0-70	927	10-2900
B ₂ horizon	14	0-40	1101	15-3500
C horizon	11	0-30	1270	15-3400

* From Presant and Tupper (1966).

Asbestos

Asbestos is a fibrous mineral occurring as a serpentine (or chrysotile) form. It is a calcium-magnesium silicate used extensively in the production of roofing material, water pipes, insulation, fireproof materials, and clothes. It is not found abundantly in the soil. If it were, it still would not offer a hazard to man, except when it becomes highly subdivided as a windborne polluting dust. The dust from processing and mining of serpentine provides a serious respiratory hazard. Soils filter-out asbestos readily on or near the surface. During soil formation, the rate of

TABLE 4.6. RANGES OF TOTAL Fe, As, Cu, Mn, Pb, Sb, Sn and Zn FOUND IN VARIOUS PODZOL, AND PODZOL-LIKE SOIL PROFILES OF HUMID TEMPERATE CLIMATE

Horizon	No. of samples	pH	Org. carbon	Fe	As	Cu	Mn	Pb	Sb	Sn	Zn
			-----%	-----				-----ppm			
A ₀₀	2	3.0-4.5	nd	.09	15	<5-15	<80-1000	10-20	<1-2	nd	60
A ₀	20	2.4-5.8	23-43	.15-4.7	5-970	<5-140	<80-3100	15-5.50%	<1-24	.7-43	20-2000
A ₂	19	3.2-4.8	.27-3.2	.7-7.2	5-1900	<5-120	<80-4600	10-2900	<1-75	1.3-136	10-1800
B ₁	19	3.4-5.4	.17-1.7	2.7-10.3	10-2900	<5-130	<80-1200	10-2600	1-110	.4-120	10-3300
B ₂	18	3.8-6.2	.07-1.8	3.9-13.4	5-3500	8-300	<80-1160	10-3.30%	1-152	.3-127	70-4600
B ₃	1	4.0	0.06	7.40	280	360	nd	4.60%	94	123	220
C	13	4.4-6.6	.05-.59	1.1-11.3	5-42 0	5-270	<80-2780	10-1.3%	<1-33	1.1-126	70-5100
C ₁	4	4.6-5.6	.13-6.8	3.6-9.9	15-500	15-560	<80-4880	60-1600	1-15	.2-8.6	70-4000
C ₂	4	4.1-6.9	.10-.57	4.2-13.5	5-200	15-80	<80-1160	20-2100	1-2.3	.1-14	90-1700
C _{g1}	2	3.8-6.9	.15-.62	.8-4.5	30-95	10-25	<80-470	360-3000	3-61	3.2-117	100-1000
C _{g2}	1	3.2	0.06	2.5	80	15	<80	3.1%	43	15	360

* Summarized data from Presant (1972); nd = not determined.

TABLE 4.7. SOME TRACE ELEMENTS FOUND IN ROCK SAMPLES*

Sample No.	-----ppm-----										-----%-----	
	Pb	Cu	Zn	As	Sb	Mn	Ag	Sn	Cd	S	Fe	CO ₂
7e	50	10	440	85	4	6,120	0.9	9.0	3.9	<200	4.41	0.49
15e	400	20	570	70	35	1,240	1.0	<0.5	@	<200	4.62	1.54
19e	560	45	170	85	3	620	13.0	62.0	24.0	<200	1.12	3.72
21d	40	35	120	5	1	465	0.2	<0.5	@	1,400	4.97	<.01
30f	75	45	190	80	3	1,320	1.1	<0.5	@	1,500	3.64	<.01
38e	15	20	30	<5	<1	<80	0.2	0.7	@	2,100	1.40	6.00
40h	5	40	100	15	1	80	0.8	2.8	@	<200	3.71	0.10
44h	<10%	150	220	1,500	280	390	67.0	14.0	@	< 3%	32.13	0.05
52d	15	5	30	@	1	390	0.1	11.0	@	200	4.34	<.01
53e	240	75	50	105	6	2,320	4.6	4.4	@	600	3.50	0.02
55e	30	15	60	25	2	775	0.3	15.0	@	2,900	3.99	0.06
62g	25	10	30	20	1	<80	0.2	4.3	@	<200	1.75	<.01
64f	15	<5	20	10	<1	700	0.1	19.0	@	<200	0.63	<.01
72d	5	5	60	35	<1	775	0.2	9.1	@	<200	2.87	<.01
73g	<5	<5	30	20	<1	540	0.2	0.7	@	600	6.44	0.01
78f	<5	30	110	@	2	1.20%	0.2	2.6	@	<200	10.22	0.24
80e	1.10%	2,100	220	1%	90	230	31.0	47.0	@		40.15	

* From Present (1971)

@ Not determined.

TABLE 4.8. CONCENTRATIONS OF TRACE METALS IN IGNEOUS AND SEDIMENTARY ROCKS, SEAWATER, AND SOILS*

Trace element	Concentration in igneous rocks, sedimentary rocks, seawater	Concentration in soils	Annual uptake by grasses and crops
	ppm	ppm	Kg
As	2 1-3 3×10^{-3}	0.1-40	10^7
B	10 20-100 4.6	2-100	10^8
Cd	0.2 0.03-3 1.1×10^{-4}	0.01-7	10^7
Cr	100 10-100 5×10^{-5}	5-3000	10^7
Co	25 1-20 2.7×10^{-4}	1-40	10^6
Cu	55 5-45 3×10^{-3}	2-100	10^8
Pb	12.5 5-20 3×10^{-5}	2-200	10^7
Ni	75 2-70 5.4×10^{-3}	10-1000	10^7
Se	0.05 0.1-1.0 9×10^{-5}	0.1-2.0	10^7
Zn	70 10-100 0.01	10-300	10^9

* From Allaway (1968)

movement of clay-sized ($< 2\mu$ diameter) particles is about 1-10 cm/3,000-40,000 yr, Berkland (1974), depending on the texture. Asbestos particles of this size would not be expected to migrate more rapidly, and particles of a larger size would move more slowly, if at all. Asbestos weathers slowly. The meager weathered products offer no more hazard to underground waters than natural silicates in soils or clay minerals.

Beryllium

Beryl is the principal Be-bearing primary mineral, although phenacite, chrysoberyl, and bertrandite are more or less widespread. The beryllium content in beryl is about 5%. Most sedimentary rocks have small amounts of beryllium. According to Beus (1956), Kuroda (1956), and Sidgwick (1950), the Be content of the earth's lithosphere varies from 0.006 to 0.002%. Soils, where there is no beryllium in the parent material (and these are most common), contain no beryllium in concentrations detectable by the usual atomic absorption spectrophotometer methods, Romney and Childress (1965). Beryllium appears to be dispersed or dissipated by the process of weathering.

Cadmium

Cadmium is a normal constituent of soils in trace or trace-trace amounts. It is present in insoluble form as an impurity in various primary and secondary minerals. The spodic soils of the New Brunswick area in Canada contain < 3 ppm, except where the soils overlay a sulfide vein; Presant (1971), for example, found more than 3 ppm in the B₂ and C horizons of two soils.

Cadmium is a normal constituent of marine deposits and is a notorious contaminant in phosphate rock. It carries through the refinement of phosphorus and appears as a superphosphate fertilizer, Lagerwerff (1972). Soil contamination takes place from automobile traffic (tires and oil), factories and mines handling zinc, use of fungicides, and certain phosphate

fertilizers. Cadmium becomes more concentrated than zinc in the air-soil-plant cycle.

Cadmium, like zinc, unites readily with sulfur, Fairbridge (1972). Also like zinc, sulfides and sphalerites are the principal carriers of cadmium. Geochemically, though, it is the nature of Cd to be widespread as isomorphic impurities in various other minerals, usually as sulfides. Cadmium sulfide weathers more slowly than zinc sulfide. Oxidation of the sulfide to sulfate causes cadmium to leach out of sulfide deposits since the sulfate is relatively soluble in acid waters. In fact, according to Hawkes and Webb (1962), Cd in streams has been a pathfinder in the geochemical search for zinc. In weathering, Cd follows Zn, except in cases of zinc sulfide. Secondary CdS remains after zinc has been leached. Fairbridge (1972) suggests that the average concentration of Cd in soils is ~ 0.5 ppm.

Chromium

Chromium in the earth's crust is derived from deeper levels in the mantle as a constituent of basaltic magmas, Smith (1972). Chromium precipitates from the magmas at an early stage as chromium spinel or in silicate minerals. Chromite resists chemical weathering. When it is released, it concentrates mechanically in laterites or heavy mineral placers. Because chromium goes into solution sparingly, it appears only in very low concentrations in precipitates and evaporates, Smith (1972). Although it appears to be fairly abundant in the earth's crust, chromium seems to occur naturally in soils, like cadmium, only in trace amounts or not at all (last 2 columns, Table 4.9). For example, chromium was positively identified in only 8 of the 68 soil samples representing 30 soil series in California (Table 4.10). The California locations may or may not be representative of general chromium distribution patterns in most soils. Unfortunately, such data are limited.

TABLE 4.9. ABUNDANCES OF ELEMENTS IN TYPICAL HUMID TEMPERATE REGION MINERAL SOILS*

(The values shown are estimates which vary widely between soils, but ranges are thought to be representative for well aerated soils of pH 6-7. Extractable indicates adsorbed or exchangeable forms. Soluble represents concentration in soil solution.)

Element	Chemical notation	Approximate concentration in ppm (mg/1000 g) or %			
		Earth's crust (total)	Mineral soil (total)	Mineral soil (extractable)	Mineral soil (soluble)
		ppm or %	ppm or %	ppm	mg/l
<u>Group one</u>					
Lithium	Li	65	5-200		
Sodium	Na	2.8%	0.15-1.5%	25-120	0.5-5
Potassium	K	2.6%	0.75-2.4%	20-200	1-10
Nitrogen	(NH ₄ ⁺)			10-100	
Rubidium	Rb	280	20-800		
Cesium	Cs	3.2			
Magnesium	Mg	2.1%	0.2-0.6%	120-600	5-50
Calcium	Ca	3.6%	0.3-1.5%	750-3700	30-300
Strontium	Sr	150	50-1000	0.2-10	
Barium	Ba	430	100-5000		
<u>Group two</u>					
Chlorine	Cl	480			60-600
Sulfur	S	520	250-1000		50-500
Selenium*	Se	0.09	0.1-2.0		0.001-0.01
<u>Group three</u>					
Fluorine	F	800	300	10-40	0.1-0.5
Phosphorus	P	1200	100-1000	0.2-20	0.002-0.03
Molybdenum	Mo	2.3	0.2-5	0.02-0.2	0.001-0.01
Silicon	Si	27.7%	29-38%		10-50
Arsenic*	As	5	1-50		
Boron	B	10	2-100	0.1-5	
<u>Group four</u>					
Aluminum	Al	8.1%	3.2-6.9%	< 25	< 0.01
Beryllium*	Be	6	0.2-10		
Vanadium	V	150	20-500	0.05-5	
<u>Group five</u>					
Iron*	Fe	5%	1.4-4.2%	< 5	very low
Manganese	Mn	1000	200-5000	5-100	0.1-10

Table 4.9 (continued).

Element	Chemical notation	Earth's crust	Mineral soil	Mineral soil	Mineral soil
<u>Group six</u>					
Copper*	Cu	20	2-100	0.05-5	0.03-0.3
Cobalt	Co	40	1-50	0.5-4	
Zinc*	Zn	80	10-300	2-30	< 0.005
Nickel	Ni	100	5-500	0.1-5	
Cadmium*	Cd	0.2			
Lead*	Pb	16	2-200	0.05-10	
Mercury	Hg	0.5	0.02-0.2		
Chromium*	Cr	200	5-1000	0.01-4	
Silver	Ag	0.02	0.1-1		
<u>Group seven</u>					
Total organic matter			0.4-10%		
Organic-N			0.02-0.5%		
Organic-P			50-500		
Organic-S			125-500		

* From Murrmann and Koutz (1972)

Values not given when a reasonable estimate could not be formulated.

Copper

The abundant stable minerals of copper in soils are sulfides. The occurrence of copper as a native element is not infrequent in terrestrial environments. It is largely held in the Cu^{++} adsorbed state. Though copper appears in the soil solution, its abundance is dependent upon whether (a) the amount of Cu exceeds the adsorption capacity of the soil, and/or (b) conditions are acidic and oxidizing. Krauskopf (1972) suggests that copper remains fairly close to its source (parent material in soils. Yet concentrations in soils do not appear to correlate with the lesser concentrations of Cu in ordinary rocks.

Copper also is abundantly present in the organic horizon of soils and is probably associated with organic matter. Total copper concentrations in

TABLE 4.10. DATA FROM ANALYSES OF 68 SOIL SAMPLES REPRESENTING 30 SOIL SERIES IN CALIFORNIA*

Elements	Positive Occurrences in samples	Concentration of saturation extracts			
		Units	Range	Mean	Median
Fe	65	ppm	< 0.01-0.8	0.05	0.03
Mo	32	"	< 0.01-22.0	0.73	< 0.01
Mn	26	"	< 0.01-0.95	0.17	< 0.01
Cu	67	"	< 0.01-0.20	0.04	0.03
Zn	68	"	0.01-0.40	0.07	0.04
Ni	30	"	< 0.01-0.09	0.02	< 0.01
Co	2	"	< 0.01-0.14	0.06	< 0.01
Cr	8	"	< 0.01-0.017	0.01	< 0.01
Hg	47	"	0.0002-0.0109	0.0024	0.001
Pb	19	"	< 0.01-0.30	0.05	< 0.01
V	39	"	< 0.01-1.20	0.07	0.01
B	16	"	< 0.1-26.0	3.06	< 0.1
Sr	51	"	< 0.1-10.4	0.93	0.18
Ba	42	"	< 0.05-1.20	0.26	0.10
Si	68	"	0.20-24.0	5.0	3.50
Ti	0	"	< 0.1-	< 0.1	< 0.1
Al	3	"	< 0.1-0.60	0.4	< 0.1
Mg	68	"	0.4-400.0	38.0	12.4
Ca	68	"	1.0-930.0	128.0	60.0
Na	68	"	0.9-19,200	524.	45.
K	68	"	0.7-128.	20.	10.
Li	27	"	< 0.03-1.08	0.11	0.05
SO ₄ sulfur	68	meq./l	0.025-145.4	8.4	1.23
Cl	68	"	0.01-580.0	12.6	0.7
Ca	68	meq./100g.soil (exchangeable+soluble)	2.8-42.0	13.3	11.0
Mg	68	"	0.19-18.0	4.4	2.9
Na	68	"	0.02-40.0	1.6	0.25
K	68	"	0.12-3.2	0.8	0.6

* From Bradford et al. (1971)

humid spodic or spodic-like soils range from a few ppm to over 360 ppm (Table 4.6) and up to 200 ppm in soil studied by Allaway (1968, Table 4.8). The mean for 84 samples as related to the A₀, A₂, B₁, B₂, and C horizons were 29, 19, 24, 61 and 92 ppm, respectively (Presant, 1971). Water-soluble Cu usually was 0.01 ppm or less, for most of the soils (Table 4.9). According to the Allaway (1968) review, soils contain between 2 and 100 ppm Cu (Table 4.8). Podzolic soils of eastern Canada contain 1.06-19.03 and 0.09-0.46 ppm exchangeable and water-soluble Cu, respectively. Small bag samples of Canadian humid soils varied in median values of total Cu from 8 to 20 ppm, Presant (1971), Table 4.11. Bradford et al. (1971) report 0.01-0.20 ppm Cu in 67 California samples (Table 4.10).

TABLE 4.11. TOTAL COPPER LEAD, AND ZINC IN SOME HUMID TEMPERATE REGION SOIL PROFILES

(Median values only)*

Horizon	Number of soil samples analyzed	pH and Total Element Concentration			
		pH	Cu	Pb	Zn
				-----ppm-----	
A ₀	48	4.2	10	25	70
A & A ₁	9	4.7	10	25	110
A ₂	48	4.1	8	15	25
B	7	4.8	20	260	140
B ₁	48	4.6	8	20	80
B ₂	48	4.7	20	20	120
C	49	4.9	25	25	100

* Summarized from data of Presant (1971).

Cyanide

Cyanide is not a natural constituent of soil. Plants can manufacture quite large amounts of cyanide in their tissues under certain climatic conditions. Incorporation of cyanide-containing plant materials into soils usually transforms CN into harmless nitrogen gas N_2 or into nitrate by microbial oxidation.

Lead

All soils contain some lead. Total lead content of soils is far greater than water-soluble lead or lead in the soil solution (Table 4.10 and 4.11), and the mean value for the earth's crust is reported to be 16 ppm (Table 4.9). Native soil lead may be substantially higher, 40-70 ppm, Davies (1968). Surface values of lead increased substantially during recent years as a result of human activity. Lead enters the soil from aerial deposits originating from automobile exhaust, fertilizers, and pesticides.

Lead-bearing soil minerals contribute substantially to lead in some soils as plants recycle and concentrate lead in the organic matter. Swaine and Mitchell (1960) report that a Scottish soil contained 20-30 ppm Pb in lower horizons as compared with 550 ppm in the surface organic layer.

Environmental conditions largely control the behavior of lead in soils during weathering. Soils, therefore, have highly variable lead contents (2-200 ppm), Wampler (1972). Waterlogged soils and those under reducing conditions contain lead in the highly insoluble PbS form. In oxidized conditions Pb appears primarily as a sulfate, which is only slowly soluble. Acidic waters carry small amounts of Pb in solution, probably as sulfate. In neutral and slightly alkaline media, Pb hydrolyzes and coprecipitates with hydroxides. Clay minerals also absorb Pb. Lead, therefore, is one of the less soluble elements in the soils.

Mercury

Estimates of Hg concentrations in soils range from 10 to 500 ppb in Sweden (Andersson, 1967). Pierce, Botbol, and Learned (1970) consider 100 ppb to be a good average figure in the USA, and Andersson (1967) suggests 60 ppb as an average in Sweden. Shacklette, Boerngren, and Turner (1971) in a study of 912 soil samples found averages of 96 ppb in eastern US, 55 ppb in western US, and 71 ppb nationwide. Local areas are much higher in Hg. In belts along major faults, natural (geological) Hg in the soil solution and water-soluble Hg are much lower than total Hg. In contrast to Sweden's 60 average total Hg, drainage water from 36 cultivated soil samples contained concentrations ranging from 0.02 to 0.07 ppb (Wiklander, 1969).

Mercury in soils under anaerobic conditions, such as expected beneath leachate of landfills, aqueous lagoons, trenches, and ponds, is converted, in part, into soluble monomethyl or gaseous dimethyl Hg complexes. Under the usual aerobic soil conditions, mercury exists in any form.

Selenium

Selenium in soils has been studied so extensively, a map showing geographic concentrations has been produced (Figure 4.6). Selenium notoriously is known as a natural soil contaminant. According to data from Murrmann and Koutz (1972), total Se concentrations in typical humid temperate region mineral soils range from 0.1 to 2.0 ppm (Table 4.9). Concentration in the soil solution (soluble Se) ranges from 0.001 to 0.01 ppm. Native levels of "available" Se in soils are sufficiently high to accumulate in plants at levels that are toxic to animals. On the other hand, Se is a required animal nutrient and some soils do not contain sufficient quantities to produce plants to satisfy animal requirements. Excesses of soil Se occur primarily in soils of neutral to alkaline pH levels and where lime (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) appear in the soil profile. In highly localized areas of the Great Plains and Rocky Mountain states,

concentrations exceed 50 ppm (Figure 4.6).

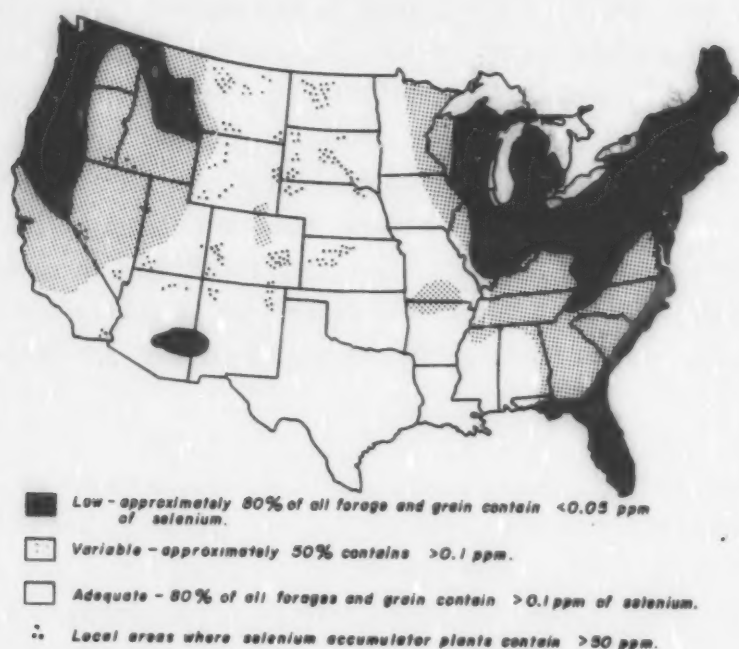


Figure 4.6. Geographic distribution of low-, variable-, and adequate-Se areas in the USA. (From Kubata and Allaway, 1972.)

Good reviews on selenium have been produced by Kubota and Allaway (1972); Rosenfeld and Beath (1964); Anderson, et al. (1961); and Moxon, Olsen, and Searight (1939).

Zinc

All soils are considered to contain Zn naturally. The Zn concentration in most soils ranges between 10 and 300 ppm. Maximum concentrations have been reported at levels between 4,000 and 6,000 ppm (Table 4.6). The availability of Zn as a required trace element for plant growth, however, often is low in some soils, and deficiency symptoms appear. Addition of

soluble Zn in soils varies widely. Where sphalerite and sulfides occur as parent material for soils, Zn is abundant. In most profiles Zn shows a rather uniform distribution throughout. Zinc differs from the other heavy metal cations in being one of the least readily absorbed.

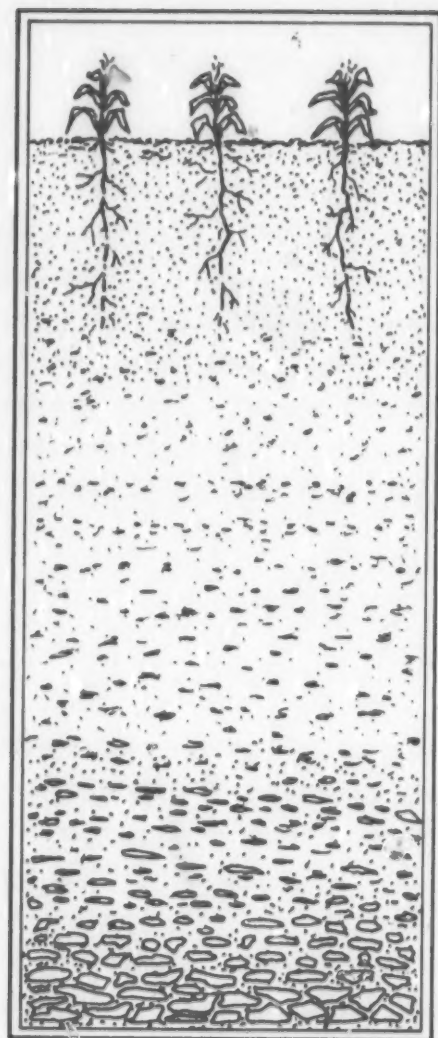
Zinc concentrations in some soils are reported in Tables 4.6 and 4.8-4.11.

Research on the oxidative weathering of sulfide ore bodies is the primary source of knowledge concerning the process of weathering and sedimentation. Zinc sulfate is relatively soluble and moves rapidly in aqueous transport. This is evidenced by the fact that sea water can contain as much as 0.01 ppm and Zn deposits in sea and lake sediments have been found at levels well over twice those of the estimated average crustal abundance or mean shale content. The great affinity of Zn for the sulfide phase, however, keeps the mobility somewhat in check (C.D. Curtis, 1972).

THE GEOLOGIC MATERIAL

Soil Formation

Soils develop slowly from geologic material, either consolidated or unconsolidated. The soil is a natural body synthesized in profile form from a variable mixture of broken, weathered minerals and decaying organic matter, which covers the earth in a thin layer. See Figure 4.7 for a representative soil profile. The most prominent factors which function in this transformation of rock into soil are (a) climate, (b) organisms (including all life--animal, vegetation, and man), (c) topography, (d) parent material, and (e) time. When rain is limited, these factors act slowly. Chemical dissolution of geologic minerals and movement of substances in and out of the soil profile, or parts of the profile, are almost at a standstill under arid conditions. Figure 4.4 shows this relationship with geologic materials. Under humid conditions such processes are accelerated.



A HORIZON

*SURFACE SOIL
ZONE OF MAXIMUM ORGANIC
ACCUMULATION. COINCIDES
MORE OR LESS CLOSELY WITH
FURROW SLICE*

B HORIZON

*SUBSOIL
CHARACTER IS DETERMINED
TO A CONSIDERABLE DEGREE
BY NATURE OF SOIL
FORMING FORCES*

C HORIZON

*SUBSTRATUM
USUALLY MORE OR
LESS WEATHERED*

Figure 4.7. A typical soil profile.

The selected potentially hazardous elements (As, Be, Cd, Cr, Cu, Fe, Pb, Hg, Se, Zn), cyanide, and asbestos are governed in their distribution and behavior toward other materials making up the earth, including soil and vegetation by the laws of geochemistry. Unfortunately, the knowledge of geochemistry as it relates to the migration of elements through geologic material is incomplete. The small amount of information available in the literature may be of some assistance, however, in understanding in a speculative way the migration of certain elements and substances.

Distribution of Elements

The distribution of Fe, Cu, and Zn and other potentially less hazardous pollutants in some common geologic materials, compared with soils (average figure), is given in Table 4.12. Because of the variability of all materials appearing in the table, the average concentration is probably reliable only within a factor of 2. Among igneous rocks these metals are more abundant in basaltic lavas than in granites. The average concentration in the earth's crust is roughly the mean of that in granite and basalt. The two kinds of igneous rock are the principal components of the earth's crust. According to Krauskopf (1972), "Soils, like shale, should have on the average a composition close to that of the earth's crust as a whole," and the numbers in Table 4.12 show general agreement with this expectation. But the raw material from which soils are derived is so variable in composition, and soil-forming processes are so different from one climatic regime to another, that an average soil composition can have little significance. The wide ranges suggested in the table include the majority of soils but certainly not the extremes. The chief importance of such ranges is simply to identify soils having concentrations outside these limits as probably anomalous either in their parent materials or in the geologic processes by which they were formed.

The contribution that geochemistry now can make to knowledge about migration of the designated hazardous pollutants through soils is very limited. The concept just put forth (Krauskopf, 1972) does serve to point

TABLE 4.12. ABUNDANCES OF MICRONUTRIENT ELEMENTS*

Element	Crust	Igneous rocks [@]		Sedimentary rocks [#]			Soils ^{**}
		Granite	Basalt	Limestone	Sandstone	Shale	
-----ppm-----							
Fe	56,000	27,000	86,000	3,800	9,800	47,000	10,000-100,000
Mn	950	400	1,500	1,100	10-100	850	20-3,000
Cu	55	10	100	4	30	45	10-80
Zn	70	40	100	20	16	95	10-300
Mo	1.5	2	1	0.4	0.2	2.6	0.2-10
B	10	15	5	20	35	100	7-80

* From Krauskopf (1972).

[@] From Taylor (1964).[#] From Turekian and Wedepohl (1961).^{**} Compilation from many sources.

out the complexity of the subject and the serious need for development of considerably more information in both soil science and geochemistry before attenuation and migration of heavy and trace elements in soils and geologic material can be predicted with accuracy. The predictions we now make, however, can serve as a departure for further investigations.

Information on the attenuation of potentially hazardous pollutants through geologic materials assumes importance because (a) many landfills and waste disposal excavations are located below the soil body and in unconsolidated material and (b) leachates which originate in soil sites often must pass through unconsolidated geologic material before reaching the capillary fringes of groundwater. Unfortunately, the geologic material located below disposal sites often is composed of sand, gravel and/or alluvial stone and debris with little or no attenuating capacity. Site locations in the stony alluvium of river bottoms can be expected to sieve-out only the larger particulates. Soluble constituents and colloidal material in this debris will pass directly into the underground water virtually unchanged.

Abundance of Elements

Because the data in Table 4.12 overemphasize mean similarities between soils and geologic material, it is important to point out that underlying rock has been claimed to have little influence on the composition of the more mature soils; i.e., soils having almost identical profile characteristics may have been derived from different parent geologic material. Soil scientists generally conclude from studies of soil-forming processes that trace nutrient elements in soils are not closely related to their concentration in parent rock, except in places where weathering of the rock is slight (Table 4.9). Suggested ranges of iron, copper, and zinc in representative surface soil are compared in Table 4.13.

Mobility of Elements

Thus, elements within the soil profile are not necessarily (in fact, rarely) found in the same proportion as they appear in the geologic materials

TABLE 4.13. THE RANGE IN MICRONUTRIENT CONTENT COMMONLY FOUND IN SOILS AND A SUGGESTED ANALYSIS OF A REPRESENTATIVE SURFACE SOIL.*

Nutrient	Normal Soil Range		Suggested Analysis of a representative surface soil
	%	ppm	
Iron	.500-5.000	5000-50,000	25,000
Manganese	.020-1.000	200-10,000	2,500
Zinc	.001-.025	10-250	100
Boron	.0005-.015	5-150	50
Copper	.0005-.015	5-150	50

*Estimates based on published data from a number of sources, especially R. L. Mitchell, "Trace Elements," in F.E. Bear, Chemistry of the Soil (1964).

from which they are derived. They either concentrate or disperse, depending on the intensity of the factors controlling mobilization within the soil body. Writers in the field of soil science have attempted to define these factors. Brooks (1972), on the other hand, gives us the view of the geochemist. He states that mobilization and distribution of the elements within the soil profile are controlled by four main factors:

1. Mobilization due to breakdown of soil minerals by various weathering agents and leaching through the profile.
2. Adsorption of ions onto clay minerals and humus.
3. Surface enrichment of elements by plant materials (the biogeochemical cycle).
4. Mobilization or fixation by soil microorganisms.

It is good to note that Brooks' statement of factors believed to influence mobility of elements in soils, though very broad, is similar to that suggested by soil scientists. His discussion comparing the importance of the individual factors also relates well to the concept put forth by soil scientists. Rules for the biogenic enrichment of elements in the soil profile as suggested by Irving and Williams (1953) are worthy of describing

here, even if only briefly. The stability of complexes between metals and organic matter is (a) largely independent of the ligand, (b) for divalent cations follows the order: $Pt > Pd > Hg > UO_2 > Be > Cu > Ni > Co > Pb > Zn > Cd > Fe > Mn > Ca > Sr > Ba$, (c) for monovalent cations: $Ag > Ti > Na > K > Pb > Cs$, and (d) for trivalent cations: $Fe > Ga > Al > Sc > In > Y > Pr > Ce > La$.

The relative mobilities of elements in the supergene environment are given in Table 4.14. Supergene refers to mineral formation by descending waters, usually taking place below the surface. Some of the conditions in the supergene environment (e.g., oxidizing conditions in the absence of free oxygen) are unlike those encountered in the soil environment and some of the factors in attenuation of metals in the soil environment (e.g., cation exchange and biological transformations) are absent in the supergene environment. Consequently, relative mobilities of metals in the two environments will differ except when solubility is the dominating factor.

TABLE 4.14. RELATIVE MOBILITIES OF CERTAIN ELEMENTS IN THE SUPERGENE ENVIRONMENT*

Element	Environmental condition			
	Oxidizing	Acidic	Neutral-alkaline	Reducing
As	3	3	3	5
Be	4	4	4	5
Cd	3	3	3	5
Cr	5	5	5	5
Cu	3	2	5	5
Fe	5	4	4	4
Hg	3	2	5	5
Pb	4	4	4	5
Se	2	2	1	5
Zn	2	2	5	5

*Adapted from Andrews-Jones (1968), as presented by Brooks (1972).

Note: Values represent descending mobility; 1 - very high; 2 - high; 3 - medium; 4 - low; 5 - very low to immobile.

SECTION V

MOBILITY OF SECECTED CONSTITUENTS IN SOIL AND SPECIFIC MECHANISMS INVOLVED

This section presents a rating of the mobility in soil of selected constituents and a discussion of the specific mechanisms which control mobility. The mobility ratings are based on information from the University of Arizona study and from the literature; the discussion of specific mechanisms is based on the author's experience and on the literature reviewed in this report. The information in this section is presented as background for the recommendations in Section III to indicate the rationale and to aid users in applications to situations not exactly covered.

MOBILITY OF CONSTITUENTS IN SOIL

While the following definitions of attenuation and mobility are not as precise as desired, they do outline the concepts. A first basis for defining attenuation is the observed decrease in the concentration of a pulse or front of solute as it moves through a soil. In this case, attenuation is quantified by specifying the time or distance required for the maximum concentration of one or more of the solutes in the pulse to decrease to some fraction of the original concentration. The second basis for defining attenuation is the soil's capacity for retaining a solute and the rate at which the solute is immobilized by the soil. In this case, attenuation is quantified by calculating a mass balance for solutes in the system after attenuation has occurred or by continuous measurements of solute input and output for the system.

Although the concept of attenuation is useful in visualizing the behavior of a system, the concept of migration or mobility is often more useful in management because it can be inferred from the commonly made measurements of the distance traveled by a given concentration of solute in a fixed time or of the time required for solute to appear at a fixed distance from a solute source.

If the system is sufficiently well behaved (i.e. linear) data used to estimate mobility can also be used to estimate attenuation. A working definition of mobility is the ease with which a specific element becomes distributed vertically in soil and/or weathered geologic materials as a function of the rate and direction of movement of soil solution or leachates from wastes deposited in or on the soil.

Mobility of a constituent in a particular soil is controlled by the net effect of all the soil characteristics or factors which influence mobility. While one factor, such as a high content of hydrous oxides of iron, aluminum, or manganese, may be very favorable for attenuation (decreased mobility), other factors may be so intensely unfavorable (e.g., partial pressure of O_2 or low O_2 content, coarse texture, low pH) as to dominate the reactions and allow rapid migration. Thus the mobility of a constituent in a particular soil should not be estimated by considering only one factor.

Absolute mobility, measured under laboratory conditions cannot be extrapolated, at this time, to field conditions. Hence the mobility of a constituent in soil is defined relative to other constituents. This rating of relative mobilities is generalized, and in a specific situation the order of constituents may change because the mobility of one or more of them is particularly sensitive to soil factors, such as pH or aeration status. Two examples of this may be seen in the mobility listings presented later in this section. Anaerobic soil conditions will not only alter the mobility ranking predicted for aerobic conditions but the absolute mobilities will be greater under anaerobic conditions and more nearly similar for most constituents. In the ranking presented for anaerobic conditions, a change in soil pH changes the relative positions of chromium, zinc, and selenium while affecting the ranking of the other constituents only slightly.

The terms used to describe mobility are qualitative and are not associated with actual rates of migration. For purposes of reference, however, the terms for the extremes of migration behavior may be defined as follows:

Relatively mobile - similar to the almost uninhibited movement of chloride ion, moving at the same rate as soil solution.

Immobile - similar to the rate of movement of clay-sized (< 2 μ diameter) particles in soils, 1 to 10 cm per 3,000 to 40,000 years, depending on the texture of the soil.

The two intermediate terms, moderately mobile and slowly mobile, are empirical groupings of substances which exhibit similar behavior and whose absolute rates of mobility lie between the two extremes described above.

Based primarily on information in the literature, the 12 selected constituents may be grouped as follows with respect to mobility under aerobic (oxidizing) conditions:

<u>Class</u>	<u>Element</u>	<u>Comment</u>
I	<u>Relatively mobile</u>	
	Cyanide - CN^-	Not strongly retained by the soil.
	Selenium - HSeO_4^- SeO_3^{2-}	Not strongly retained by the soil, at normal pH levels.
II	<u>Moderately mobile</u>	
	Iron, zinc, lead copper	Absorbed more strongly by the soil in the order of $\text{Cu}^{++} > \text{Pb}^{++} > \text{Zn}^{++} < \text{Fe}^{++}$. Stability for complexes of any given type should be increasing in the order of Fe Zn Pb Cu
	Beryllium - Be^{++}	Chemistry in soils probably similar to aluminum.
III	<u>Slowly mobile</u>	
	Arsenic - H_2AsO_4^-	Mobility similar to phosphorus.
	Cadmium - Cd^{++}	Forms insoluble precipitates in oxidizing conditions.
	Chromium - Cr^{+++}	Forms insoluble precipitates in oxidizing conditions.
	Mercury - Hg^{++}	Retained in the surface layer of most aerated soils.

<u>Class</u>	<u>Element</u>	<u>Comment</u>
IV	<u>Immobile</u>	
	Asbestos	Insoluble mineral. Particles will move at about the same rate as clays and will be retained at or near the soil surface.

Information in the literature on mobility under anaerobic (reducing) conditions is scanty. Consequently, the following estimates of mobility groupings are based primarily on results to date (1975) at the University of Arizona. Municipal landfill leachate, spiked singly with trace elements, was passed through columns of disturbed soils maintained in anaerobic conditions. The soils are described in Section III and the design of the project is described in Appendix A. The mobility of selected elements in acid soils and in neutral to alkaline soils grouped was as follows:

Soil type	pH	Elements in the leachate		
		Relatively mobile	Moderately mobile	Slowly mobile
<u>Acidic soils</u>				
Wagram l.s.	4.2			
Ava si.c.l.	4.5			
Kalkaska s.	4.7	Cadmium Nickel	Arsenic*	Copper
Davidson c.	6.2	Mercury	Beryllium	Lead
Molokai c.	6.2	Zinc	Chromium	Selenium*
Chalmers si.c.l.	6.6			
<u>Neutral to alkaline soils</u>				
Nicholson si.c.	6.7			
Fanno c.	7.0	Arsenic*	Beryllium	Copper
Mohave s.l.	7.3	Chromium*	Cadmium	Lead
Mohave _{Ca} c.l.	7.8		Mercury	Nickel
Anthony s.l.	7.8		Selenium*	
			Zinc	

* Arsenic, selenium, and to a certain extent chromium conform to the above mobility pattern least well. For example, Se was found to move slowly in Fanno c. and relatively fast through Wagram l.s. Arsenic moved slowly through the neutral soils, Nicholson s.c. and Fanno c., and relatively fast through Davidson and Molokai clays. Chromium moved slowly through

Davidson c., Nicholson si.c. and Molokai. Thus with those elements which form anions, the effect of clay content in soils is relatively dominant, particularly where the pH ranges near neutral conditions (i.e., mildly acidic or alkaline).

Specific Mechanisms

When wastes are deposited on land, a number of physical, chemical, and biological reactions take place or are initiated which affect the rate of movement of contaminants from the waste through the surrounding soil. In this section, some of the most significant of these reactions are described to lay a framework for a better understanding of the complex migration and attenuation phenomena and reaction products of the individual trace contaminants, described in other parts of this report.

Although the mechanisms have been grouped (physical, biological, and chemical) it should be understood that sharp distinctions cannot always be made between them. For example, biological processes of organic-matter degradation initiate many chemical reactions. Oxygen consumption and depletion in the substrate for carbon oxidation is one example of such specific interaction. A multitude of biological transformations of inorganic constituents also occurs in soils. Similarly, poor physical condition of the soil (heavy clays, poor structure, and compaction) dramatically influences soil aeration and related redox potential, which in turn influence biological and chemical processes.

Biological mechanisms--

Although soil microorganisms exert the primary (most significant) effect on attenuation of trace contaminants, their influence may not be immediately apparent. However, consider the following processes which soil microorganisms either perform entirely or mediate:

1. Degradation of carbonaceous wastes;
2. Transformation of cyanide to mineral nitrogen compounds and denitrification to inert N_2 gas;

3. Initiation of metal ion oxidation-reduction;
4. Production of CO_2 with subsequent formation of weakly ionized carbonic acid;
5. Production of simple organic acids;
6. Production of large and small molecular species upon which trace contaminants may be adsorbed;
7. Production of complex organic compounds which may react with trace contaminants;
8. Production of small-sized organic debris which can infiltrate small pore spaces and move downward in the soil profile.

Although it may not be possible to fully control the activities of the soil microbes, their intimate involvement in many attenuation processes is good reason to be aware of them and their role in the movement of trace contaminants.

The following excerpt from a review by Patrick Hunt (1972) is presented as an overview of microbial numbers and activities in the soil:

"The primary microorganisms of the soil can be classified as bacteria, actinomycetes, fungi, algae and soil animals. These organisms are the ecological units that may likely have the largest effect on land-disposed wastewater. The reason they are so important is that they can transform the wastewater components extensively from gases, liquids or solids; and the transformations may be beneficial or detrimental to good wastewater management. These transformations are accomplished by processes such as oxidation, reduction, mineralization, immobilization, precipitation and concentration.

"The bacteria are the most numerous and biochemically active group, especially when oxygen levels are low. They are also the smallest on a per-cell basis, commonly 1 to 10 microns in length or diameter Bacteria are primarily responsible for such important processes as nitrification, denitrification, nitrogen fixation and sulfur transformations.

"The fungi occupy more volume in the soil than any other group, and they are referred to as the most massive group. They have extensive mycelial branching and are good competitors for simple carbohydrates and bioproducts of the less efficient bacteria. The fungi are involved in humus formation, aggregate stabilization,

and certain mineral transformations. In addition, many of the plant diseases related to moist conditions are caused by fungi.

"The actinomycetes are morphologically intermediate to the bacteria and fungi. They all belong to the taxonomic order Actinomycetales, along with some of the true bacteria, and they are unicellular. However, they have mycelia that resemble those of fungi. The actinomycetes produce numerous antibiotics and are quite important to the pharmaceutical field.. Some of the thermophilic types are prevalent in rotting organic material such as animal manure, hay and compost.

"The algae are normally present in fewer numbers than the other microorganisms. However, in certain conditions, such as flooded soils, their nitrogen fixing ability is very important ecologically and agriculturally. Algae are also a prominent part of the desert ecology. They require the least number of growth factors, and the blue-green algae even fix both atmospheric nitrogen and carbon dioxide and carry on photosynthesis. Consequently they are often the first organisms to appear in a sterile soil.

"The soil animals comprise a very large group of organisms. Some of the more prominent are the protozoa, earthworms and nematodes. The protozoa are generally classified according to their mode of mobility, and are thought to be most important in their consumption of bacteria. The earthworms are quite important in maintaining the soil structure and aeration of certain soils. The nematodes have been studied mostly because of their plant parasitic role, but many nematodes are predacious or saprophagous.

"All of these microbial groups are commonly found in soils, but their numbers vary considerably and are governed by environmental conditions. Some of the more important environment parameters are temperature, moisture content, oxygen status, nutrient and energy sources, and pH.

"Soil temperatures between 25 and 35°C are best for most soil microbes. However, some organisms (psychrophiles) grow best between 0 and 20°C, while others (thermophiles) grow best at 45 to 65°C. Low temperatures tend to lengthen the generation time and slow metabolism, and high temperatures tend to speed metabolism until temperature becomes an inhibiting factor.

"A certain amount of moisture is required for biological action, but once soil moisture has increased to the point that it impedes the diffusion of oxygen in the soil it greatly reduces aerobic metabolism. When the oxygen supply of soil is low, a considerable number of microsites are anaerobic, and the populations of anaerobic microbes increase significantly.

"In order for a microbial population to expand it must have an energy source, an electron acceptor, and the essential nutrients

for its protoplasm. The autotrophs use oxidation of inorganic compounds to obtain their energy, while the heterotrophs oxidize organic compounds for energy, and the photosynthetic organisms utilize light energy. Under aerobic conditions oxygen is the electron acceptor, but under anaerobic conditions, nitrate, sulfate, or organic compounds are the acceptors. Nitrogen and phosphorus are normally the nutrients that limit microbial growth in soils, but in particular locations other nutrients can be limiting.

"The physiology of many microorganisms is quite sensitive to pH, nitrifying bacteria and certain plant pathogenic actinomycetes being the most notable. However, many microorganisms are not greatly affected by a one-unit shift to either side of their optimum pH. In soils the largest effect of pH is often the modified availability of nutrients."

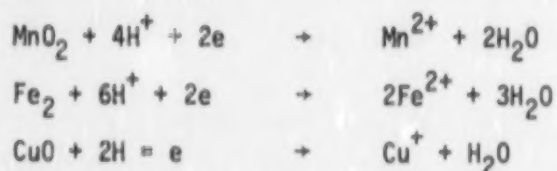
The three most important biological influences on migration and attenuation of trace contaminants (oxidation-reduction, mineralization-immobilization, and production of organic constituents) are discussed below. This grouping of mechanisms-effects, while not complete, covers most of the significant microbial involvement.

Oxidation-Reduction -- One of the most critical mechanisms of trace and heavy metal attenuation is associated with redox effect. Microorganisms in soil initiate acute reducing conditions where aeration (oxygen movement into the waste/soil) is poor and an abundant supply of "available" oxidizing substances, such as garbage, paper, or industrial organic compounds, is present.

During initial water-saturation of soils, acids and carboxyl radicals accumulate, provided that organic matter is present. The pH values generally decrease as the hydrogen activity (acids) builds up. The associated evolution of CO_2 from degradation of carbonaceous materials also contributes to hydrogen ion activity and/or lowering of pH values. Lowering soil solution pH values increases the opportunity for trace contaminants to move through soils. Oxidative processes usually have the opposite effect. Oxidizing conditions are usually associated with higher pH values than reducing conditions. Thus trace elements are expected to be less subject to

movement. However there are situations in which the two are not related. In some instances highly anaerobic and reducing conditions may be associated with the latter stages of decay or decomposition when very stable organic complexes form, and alkali earths and other basic ions accumulate.

The reduction processes in leachates, aqueous waste streams, and soils are energy-requiring systems. Decomposable carbon compounds for this necessary energy may be either organic or inorganic, but organic matter must be present for the most active reduction. Organic products resulting from the decomposition of plant and animal material are much more effective in making heavy metals more mobile under anoxic than oxic conditions. The influence of reduction on the mobility of trace and heavy metals is well documented by experimental evidence. For example, the change of Mn^{4+} , Fe^{3+} , and Cu^{2+} to Mn^{2+} , Fe^{2+} , and Cu^{+} takes place when decomposable organic materials are added to soils as follows:



Where drainage is poor in soils associated with disposal lagoons, ponds, lakes, landfills, waste water spreadings, and industrial aqueous wastestream discharges redox potentials decrease and trace and heavy metals become more soluble and mobile (Rao, 1956; Ghanem et al., 1971; Olomu et al., 1973; Hemstock and Low, 1953; Ponnampurna, 1955, 1967, 1969; Cheng, 1973).

The reduction of iron in soils is a biologically dominated process. The reaction is most prominent at low pH and anoxic conditions when readily available organic matter is present in abundance. Iron also can be used as an energy source by iron-oxidizing bacteria. Organic matter is not needed for oxidation to proceed, although some microorganisms use both.

The presence of sulfate-reducing bacteria and sulfate also favors reduction reaction of iron. The sulfide produced reduces ferric iron to

ferrous sulfide. Sulfides can cause problems in management of aqueous waste disposal because they clog soil pores. If the increased availability of iron should encounter an aerobic zone, hydroxy iron oxides precipitate.

The suggested use of anaerobic soil zones in a profile for control of nitrates through the denitrification mechanisms can create such an alternate anaerobic/aerobic layering pattern. The ubiquitous presence in soil of manganese can influence iron mobility, and like iron, clog pores and prevent the downward flow of water, Jenne (1968). Iron and manganese precipitate in a mixed system more than they do singly in pure systems, Collins and Buol (1970a,b).

Oxidation-reduction reactions of certain inorganic substances are presented in Table 5.1. Most trace contaminants can be oxidized or reduced by at least one type of microorganisms, depending on the availability or lack of oxygen and other substances in the habitat.

Mineralization and Immobilization -- When the elements or organic matter, microbial tissues, and organic complexes are converted into the inorganic state, the process is called mineralization. Biological immobilization is considered to be the reverse of mineralization. The incorporation of trace and heavy metals into microbial tissue results in their being "fixed" with mobility controlled by cell or cell tissues. On the other hand, for the elements that are relatively immobile in soils as inorganic complexes, incorporation into cell materials may be thought of as a mechanism for them to migrate as minute particles and cell materials when the tissues die and decay. Phosphorus movement in organic form is an example, Hannapel et al. (1964), and probably also arsenic by analogy. See Table 5.1 for some examples of mineralization and immobilization of inorganics.

The mechanisms of immobilization through microbial incorporation are important in the nitrogen cycle. Indeed, if this were not so, the dependent animal kingdom would long since have starved. Cyanide, for example, is oxidized in the soil into ammonium and finally into nitrate. During the transformation processes, the nitrogen is immobilized, thus

TABLE 5.1. SOME MICROBIAL TRANSFORMATIONS OF INORGANIC SUBSTANCES

(Modified from Microbial Formation and Degradation of Minerals, by Melvin P. Silverman and Henry L. Ehrlich. Advances in Applied Microbiology, Vol. 6, p. 153-206, 1964. Copyright 1964 by Academic Press. Specific references omitted.)

Element	Microorganism	Physiological activity ^a
As	<u>F. ferrooxidans</u>	As ₂ S ₃ oxidized to AsO ₃ ³⁻ ; AsO ₄ ³⁻ ; SO ₄ ²⁻ (?) ^b
	Heterotrophic bacteria	AsO ₃ ³⁻ oxidized to AsO ₄ ³⁻
	<u>Achromobacter</u> <u>Pseudomonas</u> <u>Xanthomonas</u>	
	<u>M. lactilyticus</u>	AsO ₄ ³⁻ reduced to AsO ₃ ³⁻
Cd	<u>Desulfovibrio</u>	CdCO ₃ + SO ₄ ²⁻ + 8H ⁺ + 8e ⁻ = CdS + 4H ₂ O + CO ₃ ²⁻
Cu	<u>T. ferrooxidans</u>	Cu ₂ S + 4H ₂ O = 2Cu ²⁺ + 6H ⁺ + H ₂ SO ₄ + 10e ⁻
	<u>F. ferrooxidans</u>	CuS + 4H ₂ O = Cu ²⁺ + 6H ⁺ + H ₂ SO ₄ + 8e ⁻
	<u>Desulfovibrio</u> , <u>C. nigrificans</u>	Cu ²⁺ and SO ₄ ²⁻ reduced to CuS; Cu ₁₀ S ₉ ; Cu ₂ S
	<u>M. lactilyticus</u>	Cu(OH) ₂ + H ⁺ + e ⁻ = CuOH + H ₂ O
Fe	<u>T. ferrooxidans</u> <u>Ferrobacillus</u> spp. <u>Gallionella</u>	Fe ²⁺ = Fe ³⁺ + e ⁻
	<u>Leptothrix ochracea</u> <u>Sphaerotilus</u> Protozoa, algae	
	<u>M. lactilyticus</u> <u>B. circulans</u> <u>B. polymyxa</u>	Adsorption, precipitation
	<u>Desulfovibrio</u> , <u>C. nigrificans</u>	
		Fe ³⁺ + e ⁻ = Fe ²⁺
		Fe ³⁺ + SO ₄ ²⁻ + 8H ⁺ + 9e ⁻ = FeS + 4H ₂ O
Ni	<u>T. ferrooxidans</u>	NiS + 4H ₂ O = Ni ²⁺ + 8H ⁺ + SO ₄ ²⁻ + 8e ⁻
	<u>Desulfovibrio</u>	NiCO ₃ + SO ₄ ²⁻ + 8H ⁺ + 8e ⁻ = NiS + 4H ₂ O + CO ₃ ²⁻
		Ni(OH) ₂ + SO ₄ ²⁻ + 10H ⁺ + 8e ⁻ = NiS + 6H ₂ O

Table 5.1 (continued)

Element	Microorganism	Physiological activity ^a
S	Thiobacteriaceae	$\text{H}_2\text{S} = \text{S}^0 + 2\text{H}^+ + 2\text{e}^-$ $\text{H}_2\text{S} + \text{H}_2\text{O} = \text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^-$
	Thiorhodaceae	
	Chlorobacteriaceae	
	Beggiatoaceae	
	<u>S. natans</u>	
	<u>Achromatium</u>	
	<u>Leucothrix</u> ^c	
	Bacteria,	Polysulfides reduced to thiosulfate and
	actinomycetes,	sulfide
	fungi	
	All microorganisms	$\text{S}^0 + 2\text{e}^- + 2\text{H}^+ = \text{H}_2\text{S}$
Se	<u>M. selenicus</u>	$\text{H}_2\text{Se} + 4\text{H}_2\text{O} = \text{SeO}_4^{2-} + 10\text{H}^+ + 8\text{e}^-$
	<u>M. lactilyticus</u>	$\text{Se}^0 + 2\text{e}^- + \text{H}^+ = \text{SeH}^-$
	<u>C. pasteurianum</u>	$\text{HSeO}_3^- + 4\text{e}^- + 5\text{H}^+ = \text{Se}^0 + 3\text{H}_2\text{O}$
	<u>D. desulfuricans</u>	
	<u>Neurospora</u>	
	<u>C. albicans</u>	
	Baker's yeast	
V	<u>M. lactilyticus</u>	$\text{H}_2\text{VO}_4 + 2\text{e}^- + 2\text{H}^+ = \text{VO(OH)} + \text{H}_2\text{O}$
	<u>D. desulfuricans</u>	
	<u>C. pasteurianum</u>	
Zn	<u>T. ferrooxidans</u>	$\text{ZnS} + 4\text{H}_2\text{O} = \text{Zn}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^-$
	<u>Desulfovibrio</u>	$\frac{1}{4} 2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 + \text{SO}_4^{2-} + 9\frac{1}{4} \text{H}^+ + 8\text{e}^-$ $= 5\frac{1}{4} \text{H}_2\text{O} + \frac{2}{3} \text{CO}_3^{2-} + \text{ZnS}$
Metal chelate	Heterotrophic microorganisms	Oxidation of chelating agent with precipi- tation of metal moiety

^aOxidative or reductive half-reactions listed most nearly describe the particular microbial activity cited.

^bProof of sulfate production lacking.

^cBut see Harold and Stanier (1955).

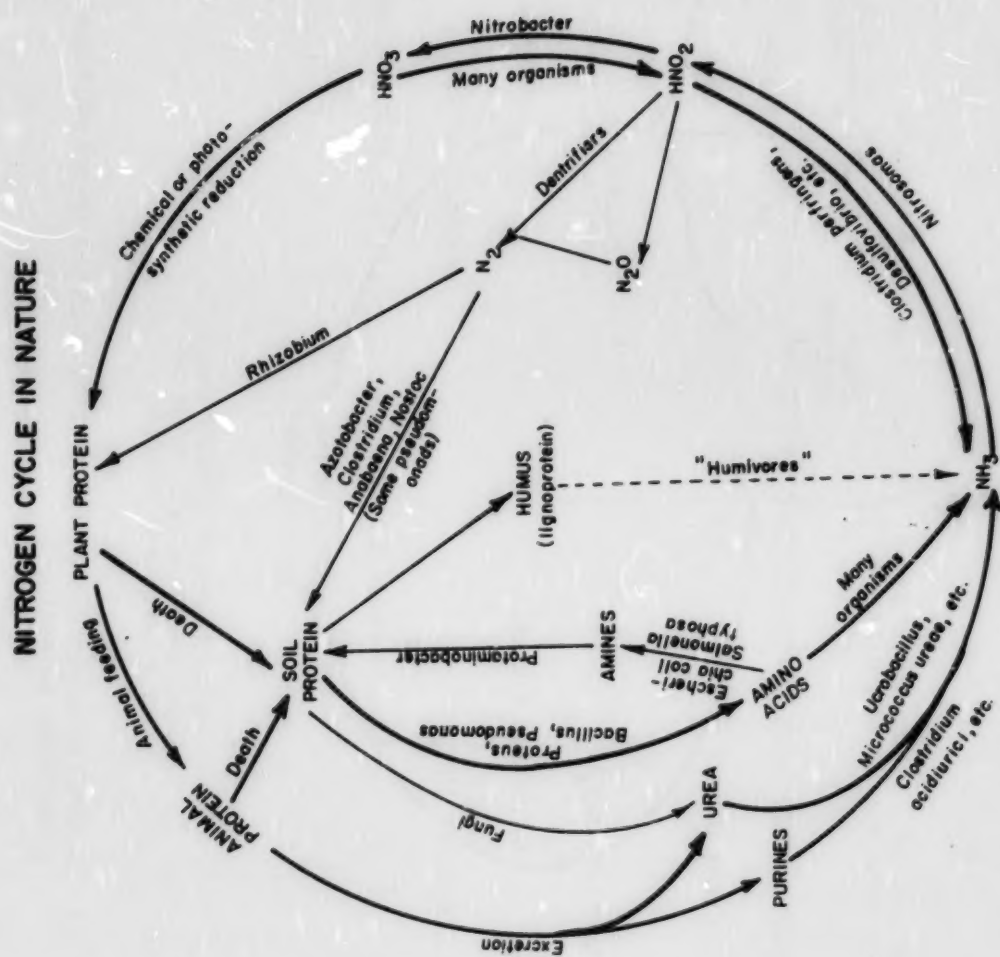
preventing it from being lost to plants by leaching. The carbon is oxidized to harmless CO_2 . As it again becomes mineralized slowly, plants have an opportunity to take up the nitrogen and combine it into their protein pool. Upon death of the cell tissues which contain protein (animal, plant, or microorganism), the N returns to the soil-organic matter pool where it slowly mineralizes into a form usable by plants again, is lost to subsurface depths by leaching, or is denitrified to N_2 gas and escapes harmlessly into the atmosphere. (Figures 5.1 and 5.2).

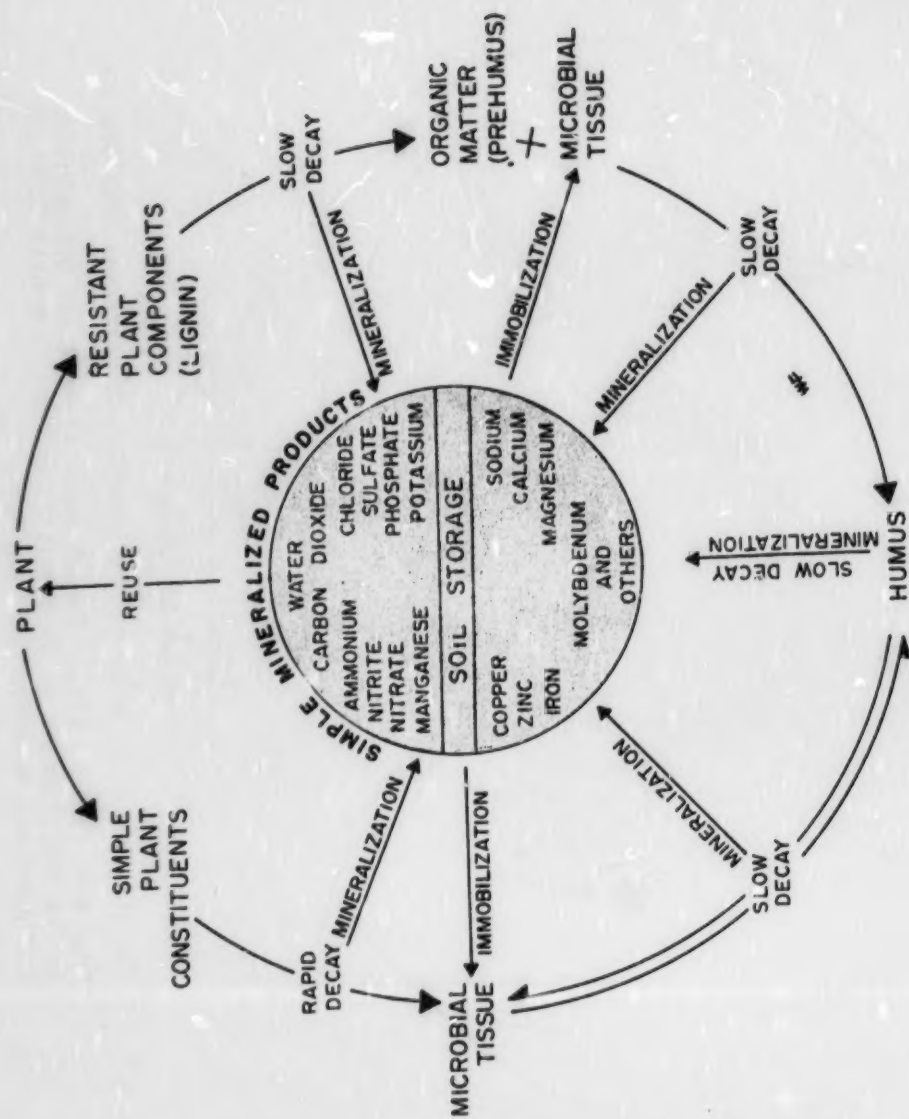
The examples of other element cycles which illustrate biological influence on mobility of elements are carbon (Figure 5.3), phosphorus (Figure 5.4), and sulfur (Figure 5.5). Such cycles could be drawn for the 12 potentially hazardous pollutants with existing data and a little educated speculation.

Since those trace and heavy metals which concern us most enter in organic combination as living cells and tissues of microorganisms of soil, plants, and animals, the biological mechanisms of mineralization and immobilization act significantly in attenuation of the potentially hazardous pollutants.

Reactions with Organic Constituents -- Organic complexes in soils which accumulate as a result of microbial synthesis as well as degradation of organic residues have a relatively high capacity to combine strongly with trace and heavy elements. Hodgson (1963), for example, delineates three organic fractions which can be identified in relation to immobility of metals:

1. Lignin-like compounds of high molecular weight and similar organics, mostly cyclic in nature.
2. Organic acids and bases, short chained in nature (short-chained humic acids included).
3. Soluble constituents which become insoluble when combining with heavy metals





THE ORGANIC MATTER CYCLE IN SOIL

Figure 5.3. The carbon cycle and organic matter cycle showing decay release of mineral nutrients and humus formation. (From W.H. Fuller. Soils of The Desert Southwest, Univ. of Ariz. Press, Tucson, AZ. 1975.)

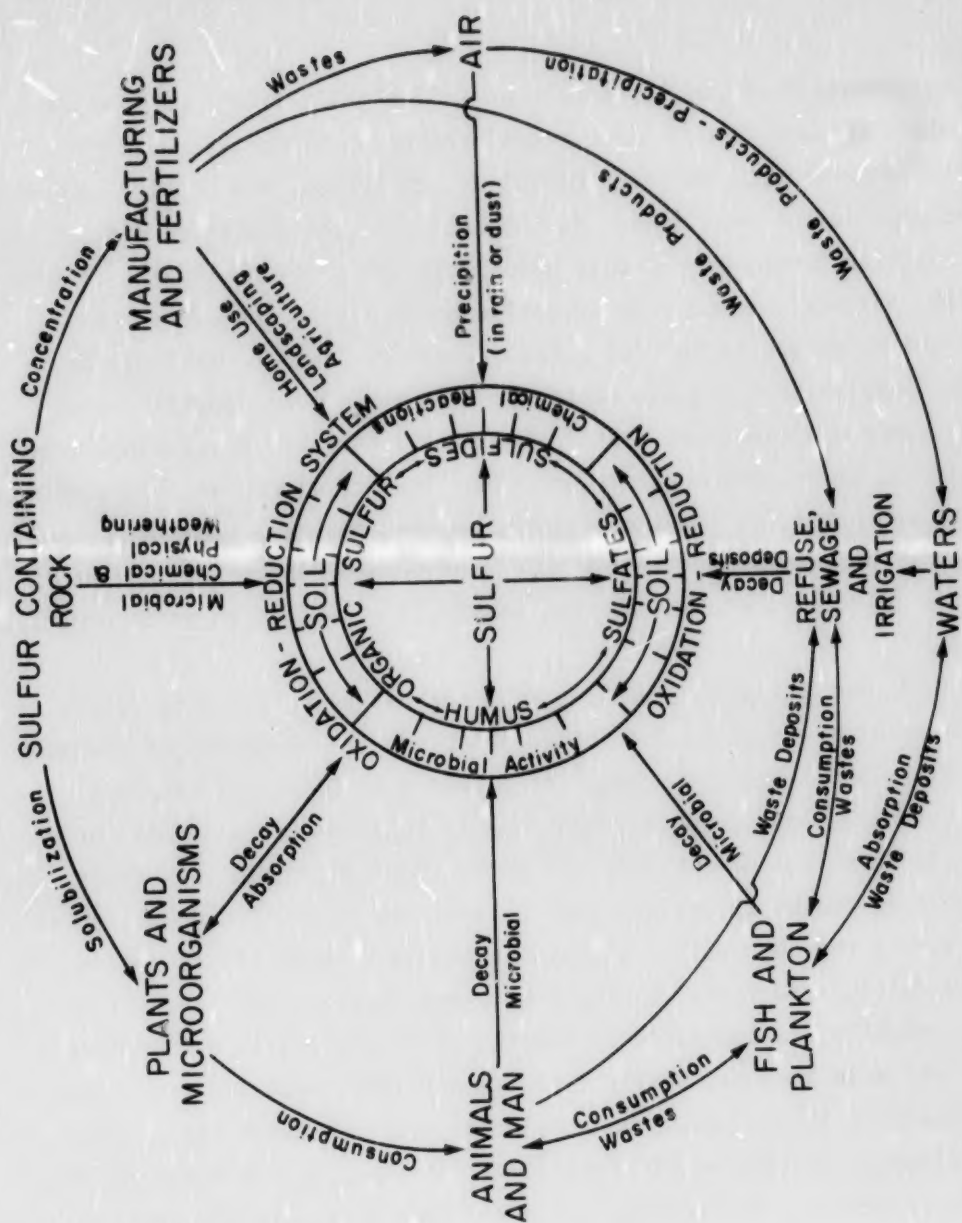


Figure 5.5. The sulfur cycle in nature showing oxidation of sulfur to sulfuric acid and sulfate formation and reduction to sulfides. (From W.H. Fuller, Soils of the Desert Southwest. Univ. Ariz. Press, Tucson, 1975.)

Organic substances, thus, are an important factor in attenuation and immobilization of potentially hazardous metal pollutants. Also see Fuller and L'Annunziata (1968), L'Annunziata and Fuller (1968), and Hannapel et al. (1964).

The formation of complexes between soil organic matter and metals can take place through several mechanisms, according to Mortensen (1963). These are: ion-exchange, surface adsorption, chelation, and complex coagulation and peptization reactions. He suggests that the chelation ligands (organic reactive groups or radicals which "tie up" or bind elements chemically in the polymeric components of soil organic matter include carboxyl, hydroxyl, and amino groups to list a few. Specific ligands which may be present not only in soil organic matter but leachates from landfills and waste from other municipal and certain industrial operations (canning, wood product manufacturing, tanning, slaughtering) include microbial slimes, gums, cell debris and humus; polymers of lignin, polysaccharides, tannins, polyphenols, proteins, quinones; and low molecular weight substances, aliphatic acids, amino acids, organic phosphates, phenolics and volatile acid complexes.

Wright and Schnitzer (1963) suggest that in podzolic soils fulvic acid is an important ligand which brings about the translocation or movement of Fe and Al. The aromatic "nucleus" of fulvic acid (with its attached hydroxyl, carboxyl, and carbonyl groups) makes it a likely candidate for critically influencing the mobility and attenuation of metals (Schnitzer, 1969). There is reason to believe that fulvic acid forms through microbial synthesis during the degradation process in sanitary landfills as well as in soils since fulvic acid forms readily from plant residues and landfill materials generally are dominated by substances of plant origin (Schnitzer, 1969). Fulvic acid then may easily find its way into leachates from these systems. There is little doubt that chelation reactions with the organic matter of disposal systems exert significant influence on the movement and attenuation of metals. Microbiological activities which are responsible for the production of the organic chelating substances are thus an important factor in attenuation of the hazardous trace contaminants in soils and geologic materials.

Organic complexes in municipal landfill leachates probably immobilize many of the trace metal contaminants by organic precipitation in the presence of air (oxygen). Some of the organic precipitates are irreversible unless the pH drops to 3.0 or below. The organic constituents in wastestreams and leachates of low pH values (3 or below) may be expected to immobilize trace contaminants poorly. The hydrogen ion concentration tends to keep heavy metals and trace elements in solution. A host of unidentified and identifiable biological products present both in soils and aqueous organic "wastestreams" is capable of immobilizing metals. Flaig (1966) and Allison (1973) discuss some of these compounds in their review concerning the retention of metals by organic constituents in soil. Suggested chemical reactions between some of the better known organic complexes and the selected potentially hazardous waste constituents will be discussed further in the section on chemical reactions.

Chemical Mechanisms--

This section reports some of the most obvious chemical mechanisms which relate to attenuation of the trace contaminants:

1. Complexing with organic substances (cation exchange, organic anion fixation, nonpolar organic reactions, and nonionic polar reactions).
2. Adsorption by mineral species (not ion exchange).
3. Chemical oxidation-reduction effects.
4. Precipitation reactions and pH effects.
5. Ion exchange reactions.

Complexing with Organic Substances-- Organic-metal complexes can be thought of as a reservoir of potentially hazardous pollutants which mineralize at various rates, depending on the susceptibility of the organic molecules to biological attack, and release the elements for migration if the environment is favorable. Since the soil, effluent, sludge, wastestream, or leachate contains a wide variety of organic compounds and complexes, the net attenuation or retention effect of this organic fraction is difficult to evaluate.

As previously discussed, aqueous wastestreams and solid waste landfill leachates contain a wide variety of organic substances capable of chemically immobilizing trace contaminants. These organic complexes also may be further degraded biologically and release contaminants (mineralization) at varying rates, depending on the biodegradability of the material. Immobilization and mobilization, thus, take place at the same time. Generally, immobilization equals or exceeds mobilization for heavy metals. Some types of the organic compounds, produced or altered by biological action, may immobilize trace contaminants by direct chemical bond complexing processes in the soil. Organic cations may attach themselves to cation exchange positions of soil clays as well as to organic matter exchange sites. Soil organic constituents, for example, possess a high cation exchange capacity, even much greater than that of montmorillonite. The large cations attach themselves to the exchange positions with varying degrees of tenacity (Stevenson and Ardakani, 1972). Some contaminants become a fixed part of the exchange material. In this manner they may reduce the total exchange capacity of the soil.

Organic anions react with such elements as Ca^{2+} , Fe^{2+} , Al^{3+} , etc., and form slowly soluble to nearly insoluble compounds. At low pH values basic bonds unite with H^+ on soil-particle surfaces.

Another interesting phenomenon or mechanism of attenuation of non-polar organic compounds (such as oils, grease, and hydrocarbons of low molecular weight which are insoluble in water) is film formation on the surface of soil particles. The author's personal experiences with fuel oil spills have been very convincing as to the great tenacity with which soils absorb and hold certain nonpolar hydrocarbons against migration through the soil. Fine-textured soils, particularly clays, because of their relatively vast surface area, have great capacity to remove and attenuate certain types of organic molecules. The effectiveness probably increases with the size and charge of the molecule.

Nonionic polar compounds in aqueous wastestreams and leachates can be retained to some degree depending on (a) their susceptibility to microbial

degradation and (b) their specific molecular characteristics.

The detailed interest in attenuation by chemical reaction with organic substances results from the knowledge that (a) wastestreams often contain substantial levels of organic molecules, (b) the soil at the disposal site often contains organic matter, and (c) organic compounds complex readily with trace and heavy metals.

Adsorption by Mineral Surfaces--The adsorption of trace and heavy metals in soils leading to immobilization may be of various types. Indeed, specific adsorption forces may often dominate the behavior of heavy metals when they make contact with soil (Tiffin, Lagerwerff, and Taylor, 1973). Adsorption may be variously defined but, in general, it is the adhesion, in an extremely thin layer of gas molecules, dissolved substances or liquids, to the surface of solids with which they are in contact, Ellis and Knezek (1972). Ion exchange is not considered here in adsorption reactions, except when the soil has a capacity to retain dissolved chemicals so tightly that they can be removed from the solid fraction only with difficulty (Murrmann and Koutz, 1972). There is some evidence (De Mumbrum and Jackson, 1956; Wilkinson et al. 1968; Hodgson, 1960) that a certain fraction of the exchange capacity is specific for certain ions (Cu, Zn, and Co). The fraction that becomes immobile is held by variable bonding strengths and a slow rate of reaction approaching first-order kinetics.

Adsorption, as discussed here, differs from precipitation, which forms well defined solid phases. The adsorption mechanisms are poorly defined and often the term is used loosely with no real meaning when no reasonable explanation can be made for interactions of chemicals with soils. Adsorption has been used at times to include the soil cation-exchange-capacity of both loosely and firmly held ions. In this report, adsorption will be considered as the adhesion of the elements in an aqueous medium, to the surface of solid materials, including layered silicates, hydroxy oxides, organic matter, and lime. Adsorption probably is the most important process influencing attenuation of the trace and heavy metals in soils. Evidence for this comes from a number of sources. The high anion retention by soils cannot be explained by

anion exchange or by precipitation, Jenne (1968). Phosphate is an example. Phosphorus is thought to react with surface iron and aluminum exposed by their layer silicates and with iron and aluminum hydroxide and hydrous oxides coating soil particles.

Another possibility is the incorporation of certain elements as impurities in solid phase accumulations and crystal structures which resist resolution. Salt formation of lime and gypsum, iron and aluminum hydroxy oxides, and other precipitates may well assume some solid phase formations that occlude trace and heavy metals as impurities.

The possibility of forming slowly soluble impurities with organic constituents should not be overlooked, although this probably should be considered as a distant "cousin" to the mechanism of adsorption.

The most interesting adsorption mechanisms in soils are those associated with iron and aluminum hydroxides and hydroxy oxides. Manganese probably should be included along with Fe and Al but there is much less evidence for such Mn reactions than for Fe and Al. A very small amount of hydrous oxides can create a great dimension of reactive surface area. Hydroxy oxides form into particles of fine (colloidal), coarse, and/or porous aggregates and increase reactive iron and aluminum adsorption surfaces, (Jenne, 1968; Jackson, 1963; and Marion et al., 1976).

Another argument favoring the dominance of adsorption reactions over the conventional ion exchange reactions is that the concentration of heavy metal cations is so low, compared with that of other ions (H^+ , Ca^{2+} , Na^+ , K^+), that mass action prevents cation exchange being the most effective means of removal of trace and heavy metals from aqueous waste solutions.

Adsorption processes take place rapidly. Rather than stopping at this initial reaction phase, though, the equilibrium continues to shift slowly toward the more insoluble forms. According to Murrmann and Koutz (1972), a general equation may be written as:

Soluble - x $\rightleftharpoons$ adsorbed - x $\rightarrow$ insoluble - x

where x represents the component adsorbed from the solution.

Chemical Oxidation-Reduction Effects--Chemical and biological oxidation-reduction reactions, as they relate to retention of the selected hazardous elements, are not often possible to separate in soils. Most oxidation-reduction reactions in soils are initiated by biological activity. The inorganic ions which are released, however, may be free to take part in a multitude of strictly chemical reactions.

Oxidation/reduction reactions would be important in a management program only if an anoxic system, such as municipal landfill leachate, could be oxidized (e.g., chemical treatment on the surface, land spreading, spray irrigation) to reduce the solubility of metal complexes and compounds. Reduced forms generally are more soluble than oxidized forms of heavy metals. A logical research "follow-up" is to try various types of field aeration systems even to placing perforated plastic tubing below fills through which air can be pumped into leachate.

Precipitation Reactions and pH Effects--The precipitation reactions of trace and heavy metals in soils relate so closely to pH levels that discussion of the two cannot be separated. It is difficult to distinguish between precipitation and adsorption reactions in soils. (Precipitation here is used in the strict chemical meaning.) Numerous literature references can be cited to the effect that trace and heavy metals, in general, form insoluble or very slowly soluble precipitates at neutral or higher pH values. Since good literature reviews already exist for this type of attenuation mechanism, Jenne (1968), Hahne and Kroontje (1973), Lagerwerff (1972), Kee and Bloomfield (1962), Lindsay (1972a) and Krauskopf (1972), none will be given here. Liming results in the formation of insoluble heavy metal compounds. More specifically, Jenne (1968) states that, "it seems apparent that the effect ascribed to sorption of zinc and copper by calcium carbonate is primarily a pH effect and, secondly, an effect of carbonate-bicarbonate ions on heavy metal solubility."

Jenne (1968) proposes that the hydrous oxides of Mn and Fe, furnish the principal control for the attenuation of Co, Ni, Cu, and Zn and, in general, other heavy metals in soil and fresh water sediments, and are, in his words, "a sink" for heavy metals. His contention is supported partly by the ubiquitous occurrence of the hydrous oxides in clays, soils, and sediments both as coatings on mineral particles and as discrete oxide particles and specific examples of hydrous oxide reactions. He suggests that sorption and desorption of heavy metals take place in response to: "(a) solution concentration of the metal in question; (b) concentration of competing metals; (c) hydrogen ion concentration; and (d) formation and destruction of organic chelates and inorganic complexes." He claims only a very small amount of hydrous oxides of Mn and/or Fe may be sufficient to control the equilibrium between the heavy metals in solid and aqueous phases. Prediction of this equilibrium is complicated by the dissolution-precipitation of Mn and Fe oxides in relation to changes in pH-Eh¹ and to leaching of Fe and Mn which may be occurring at the same time as adsorption reactions. The results furnished by Tiller, Hodgson, and Peech (1963) provide additional evidence that fixation of heavy metals is not exclusively related to cation exchange capacity. They found that by plotting cobalt sorption (from 1.1×10^{-5} M CoCl₂) vs. pH, 15 of the 16 soils are nearly identical in shape to those of manganese sorption by δ -MnO₂ of Morgan and Stumm (1964). Jenne (1968) believes there is sufficient evidence in the literature indicating that metal ion-clay mineral surface complex formation is not important, at least for Cu and Zn.

Another important factor in precipitation of trace and heavy metals which often is overlooked is concentration. Adsorption reactions seem to dominate with micro-concentrations but precipitation frequently occurs with macro-concentrations. Bingham, Page and Sims' research (1964) indicates that the dominant reason for retention of copper chloride and acetate by montmorillonite at pH values above 5.0 and 6.5, respectively, is precipitation at Cu concentrations twice the cation exchange capacity. The same Zn salts precipitated at one pH unit higher than the Cu salts.

¹Eh refers to redox potential as an intensity factor.

Still another interesting phenomenon of the hydrous oxide surfaces is that of catalyzing oxidation reactions (and thereby precipitation). Oxides of iron appear to catalyze the oxidation of Fe^{++} to Fe^{+++} , Gasser and Bloomfield (1955). The same seems to be true for Mn^{++} to Mn^{++++} , Zapffe (1931).

The pH effect on heavy metal fixation and mobility, according to Jenne (1968) can be "interpreted in terms of competitive exchange of hydrogen with heavy metals occluded by the hydrous oxides as well as dissolution-precipitation and oxidation of the hydrous manganese and iron oxides."

Some of the many investigations concerning pH effect are:

1. Soil samples sorbed less metal in more acid systems (Banerjee, Bray, and Melsted, 1953; Garrels and Christ, 1965; Gayer and Woontmer, 1956).
2. Some of the sorbed nonexchangeable heavy metal is acid extractable (Banerjee, Bray and Melsted, 1953; Crooke, 1956; Hodgson, 1963; Hodgson and Tiller, 1962; Nelson and Melsted, 1955; and Tiller and Hodgson, 1962).
3. Lowering the pH of the extractant removes more of the sorbed metal (Banerjee et al., 1953; Brown, 1950; Dion, Mann, and Heintze, 1947; Hibbard, 1940; Jones, Gall, and Barnette, 1936; Nelson and Melsted, 1955; Staker and Cummings, 1941).
4. More manganese is extracted from acidic soil (Walker and Barber, 1960; Williams and Moore, 1952).

Conversely, liming to raise the pH, decreases the solubility of many heavy metals and their availability to plants. Some references often cited are: Askew and Dixon (1937); Askew and Maunsell (1937); Camp and Reuther (1937); Carroll (1958); Christensen and Toth, and Bear (1950); Ekman, Karlsson, Svanberg (1952); Fox and Plucknett (1954); Gall and Barnette (1940); Hill, Toth and Bear (1953); Jones, Gall and Barnette (1936); Lott (1938); Mann (1930); Mitchell (1951); Page (1964); Painter, Toth, and Bear (1953); Percival, Josselyn, and Beeson (1955); Reith and Mitchell (1964); Prince and

Toth (1938); Rogers and Wu (1948); Seatz (1960); Waltz, Toth, and Bear (1953); Bear (1956).

In summary, the pH effect on the trace and heavy metals must result from the combined effect of the activity of hydrogen on:

1. The direct precipitation of the metal as the oxide or hydroxide, or carbonate (PbCO_3), for example.
2. The concentration of carbonate, phosphate and possibly silicate ions in the aqueous phases of the system.
3. The precipitation-dissolution of certain oxides, notably Fe and Mn.
4. The rate of sorption and desorption of heavy metals by the hydrous oxides.

Items 1, 3, and 4 may be very difficult to distinguish experimentally.

The pH range for maximum solubility of trace and heavy metals varies with the origin of the soil. The optimum for availability of trace metals to plants is given as 5.5-5.8 for wood-sedge soils and 5.0 for sphagnum peats (Lucas and Davis, 1961). This is 1.0 to 1.5 pH units lower than for most mineral soils. Interactions of heavy and trace metals with phosphorus in various forms (silicates and carbonates), in addition to hydrous oxides of Fe and Mn, complicate the straightforward effects of pH on their precipitation and mobility in soils. Also, not to be overlooked is Jackson's (1963) study, "Aluminum bonding: A unifying principle in soil science." The Al^{2+} ion bonds through oxygen to form a number of functional groups which influence trace contaminant reactions in soils. The layer silicate clays, for example, provide cation exchange sites. At pH values below about 5.5, Al is solubilized in soil solution (Lindsay et al., 1959). A number of pH-controlled aluminum species appear in soils which are highly reactive (Marion et al., 1976).

Ion Exchange Reactions--Ion exchange reactions occupy the bulk of attention in the soil chemistry literature. The soil chemist and plant

nutritionist "team up" to explain plant uptake, absorption, and nutrient availability through the common phenomenon of ion exchange. Laboratories throughout the world routinely evaluate soils on the basis of CEC, which is related primarily to the clay and organic matter of soils. CEC values, though empirical and originating from a multitude of soil properties (some yet to be evaluated), provide crop production people as well as plant nutritionists with valuable information. The effect of ion exchange reactions on trace and heavy metal mobility in soils is another matter. Ion exchange appears to function, in only a small way, as a temporary or transitory mechanism of attenuation. Ion exchange is a phenomenon relating to positively charged ions (cations) much more than to negatively charged ions (anions). Soil clay minerals, the primary seat of cation exchange, have small capacity for anion exchange.

The relationship of ion exchange reactions and retention of elements in soil is similar to that of a football player who receives the kickoff. As the ball carrier proceeds up the field, blockers and tacklers slow his progress but many never stop him completely. If the carrier is stopped, it is temporary. He has a number of additional chances to proceed to the goal. Ultimately the goal is reached, the tackler and blocker only relate to time delay, just as an ion will be delayed on its progress through soil by temporary contact with the exchange positions. Some ions move more rapidly than others. They are the better ball carriers. They are the more loosely held metal ions. The ion exchange complex plays an important part in time delay but usually does not inhibit the ion from arriving at some ultimate goal of depth in the soil.

Ion exchange in the mineral fraction of soil is believed to originate primarily from the exchange sites of layered silicate clays. Substitution of divalent for trivalent and trivalent for quadravalent cations within the crystal structure of the mineral can take place to a limited extent. Most layered aluminum silicate minerals (secondary) in soils possess a permanent negative charge within the crystal lattice structure. This internal negative charge presumably is balanced on the surface by positively charged, exchangeable cations.

There are four primary factors affecting the ion exchange capacity of soils: (a) kind of clay mineral present, (b) the quantity of clay mineral, (c) the amount of organic matter present, (d) the pH of the soil.

There is a great amount of information in the literature on the CEC of different clay minerals. The montmorillonite expanding lattice type has CEC values ranging from 60 to 120 meq/100 g of the exchanger phase, while the kaolinite nonexpanding lattice type has between 5-15 meq/100 g. The CEC of illite type clays is between those for montmorillonite and kaolinite.

The second factor, quantity, is reflected by soil texture. CEC usually increases with an increase in the clay content of soil. Silt also has a CEC, but the values are lower than those for clay. Sands exhibit almost no exchange capacity in relative comparison. Therefore, in general, soils have greater CEC values the finer the textural class. For example, CEC values of sandy soils may range from 2 to 6 meq/100 g; sandy loams 4 to 15; silt loams 10 to 25, and clay and clay loams 20 to 60.

The third factor, organic matter, is very prominent in enhancing the total CEC of a soil. Landfills, however, are located below the soil organic layer, though the leachate from the fill itself contains organic constituents which exhibit cation exchange capacity.

The fourth factor, pH, was discussed earlier but not in connection with CEC. The CEC, in general, increases with the soil pH. Over wide ranges, pH changes the CEC greatly. Over the range of 5 to 7, however, the increase probably does not exceed 30% of the original value, Murrmann and Koutz (1972).

In defense of the position that ion exchange in the soil is an important mechanism for the attenuation of trace and heavy metals, it is only fair to reproduce Murrmann and Koutz' (1972) discussion:

"The type of exchange capacity described above (i.e., clay minerals having layer aluminum silicate) is more or less permanent.

However, the ... material fraction of soils possesses another element of exchange capacity which depends upon the acidity or pH of the soil. This type of ion exchange is reflected in the retention of both cations and anions. The nature of pH-dependent exchange capacity of the mineral phase is not well understood but is thought to result primarily as a consequence of the dissociation or association of hydrogen ions (H^+) with structural elements at the crystal edges of aluminum silicate minerals, with the more amorphous aluminum silicate phases, and to some degree with iron and aluminum hydroxide materials. At high pH values of 8 or more, the contribution to the total cation exchange capacity can be considerable. At pH values below 4 or 5 the retention of anions such as sulfates (SO_4^{2-}) can be significant. However, in the pH range from 5 to 7 characteristic of many soils the retention of anions by this mechanism is small to insignificant. The retention of cations would normally not account for more than 10 to 20% of the total cation exchange capacity attributed to the mineral phase. However, this type of exchange capacity does account for the tendency of soils to retain anions with decreasing soil pH and, in part, for the increase in cation exchange capacity with increasing pH."

They go on to say, "Soils with a high cation exchange capacity generally also have the ability to remove heavy metal cations from solution due to adsorption by the soil inorganic and organic components. However, exchange capacity should not be equated with the capacity of a soil to remove chemicals from wastewater. Since the exchange capacity of a soil is already saturated with common cations such as Ca^{++} and Na^+ , retention of wastewater chemicals will be accompanied by the release of these cations into solution. Wastewater also normally contains large amounts of Na^+ and Ca^{++} relative to the amounts of heavy metal cations. Thus, the net effect will be some readjustment in the composition of the exchanger and solution phases but the total soluble salt concentration in the wastewater will remain fairly constant. Removal of heavy metal cations by cation exchange will be small due to the competing effects of the common cations present at

much higher levels."

From a practical standpoint, cation exchange does not effectively lower the total salt concentration in aqueous waste solutions; heavy metal cations are not significantly retained by cation exchange under soil conditions where concentrations of soluble salts in solution are much higher than concentrations of the heavy metals.

For practical purposes, the fact that fine-textured soils, in general, immobilize trace and heavy metals to a greater extent than coarse-textured soils may provide useful guidelines for disposal of trace and heavy metals, even if our knowledge of the exact proportioning of the mechanisms involved is incomplete.

Physical Mechanisms--

It is not always possible to make a clear-cut separation between physical and chemical mechanisms of element retention in soil. A few purely physical factors have roles which can be separated and discussed.

This section lists some of the physical mechanisms/ influences on trace contaminant movement in soils and discusses their interaction with biological and chemical mechanisms. The topics covered are:

1. Particle size distribution
2. Pore size distribution
3. Moisture relationships
4. Adsorption
5. Temperature

Particle Size Distribution--Soil particle-size distribution is often referred to in terms of texture classes. In general, the finer the particles (texture), the less trace contaminants can move through soils. Suspended solids in aqueous waste streams and solid waste leachates remain in the soil near the first point of contact as a result of filtering action. The dissolved solids move with the waste and percolate through the soil.

The constituents which are not attenuated or immobilized may finally reach the capillary fringes of underground water tables. Soil texture exerts a profound effect on this process, since it is an indicator of such parameters as pore (space) size and distribution, particle size, exposed surface area, clay content, organic matter, and moisture conditions.

Soil solutions (and leachates, such as those from solid waste) flow more slowly through finer soils. The intensity of attenuation, though, is not dependent only on flow rate. Two soils of nearly identical texture may not have the same attenuation characteristics since attenuation also is influenced by factors other than flux and particle size and distribution. The kind of clay mineral, presence of lime, organic matter, hydrous oxides, and other factors influence mobility and can cause differences as much as 1- or 2-fold between like-textured soils. Proportionally wider differences occur more commonly between like-textured coarse soils.

Whereas texture is thought of as being unique in any given soil, the arrangement of soil particles (structure) varies considerably. This manifests itself in the total pore space and the pore size distribution. (For a general discussion see Baver et al., 1972, and Hillel, 1971). While the measurement of total pore space is relatively straightforward, that of pore size usually involves an idealization as equivalent capillary radii, Baver et al. (1972), Vomocil (1965), Klock et al. (1969). However, if we assign a single number to total pore space, a distribution is not so simply characterized (Cary and Hayden, 1973; Sridharan et al., 1971). This is especially important since pores of different sizes contribute unequally to the flow of soil solution and the reaction of solute. Frequently it has been useful to consider the particle size as a measure of pore size distribution (Scheidegger, 1960, who also mentions the relation to surface area). This approach has been used not only to study indirectly the pore size distribution (Graton and Fraser, 1935; Bodman and Constantin, 1965), but also the movement of solute (Underhill, 1973).

The net movement of solute is the result of interaction with pores of all sizes. While we cannot simply add up these effects, it is useful to look at the movement of solute in pores having a uniform radius. The movement of unreacted solute occurs by convection (bulk transfer in solution) or diffusion. The movement of liquids through capillaries can be described by the analysis of Hagen and Poiseuille (see Bird et al., 1960), from which we conclude that the larger pores are primarily responsible for the movement of solution. We should also note that since the ratio of surface area to volume is smallest for the largest pores, the potential for attenuation is least and for migration greatest in the larger pores.

The diffusion of solute in pores is complicated by the fact that this is usually superimposed on the convective transfer. Taylor (1953) has presented an analysis which implies that the diffusion coefficient is larger in the larger pores. Following a different line of reasoning Beck and Schultz (1970) and Saxena et al. (1974), demonstrated that a reduction of diffusion coefficients occurs with a decrease in pore size. Thus the effect of diffusion is to accentuate that of convective transfer.

When we start to talk about a more realistic model for soils, we find that the capillary model is inadequate. In general, we find that the migration of nonreactive solutes is greater than we would otherwise expect. This phenomenon is labeled 'dispersion' (Greenkorn and Kessler, 1970; Nunge and Gill, 1970; Ogata, 1970; Fried and Combarous, 1971). While dispersion includes the effects of diffusion, we emphasize the effects due to the structure of the soil. Its effects can be categorized roughly as (a) those due to a random matrix of soil particles and hence, soil pore spaces, (b) those effects due to aggregates and other large structural units, and (c) those resulting from the instability of a displacing front.

The presence of a random structure in soils results in the presence of 'dead-end' pores (Turner, 1958) and tortuous flow paths (Jong, 1958; Bruch and Street, 1967; and Ogata, 1970). This may be advantageous if it enlarges the volume of soil exposed to the solute, or deleterious if it

results in premature transfer to an aquifer or stream. The work of Harleman et al. (1963) indicates that, in general, the dispersivity will be greater for coarser-textured soils. However, this may not significantly affect attenuation by such soils.

The presence of aggregates or extensive cracks and ped formation¹ may result in the primary movement of soil solution between these structures rather than through them. In general, the result is a decrease in the efficiency of mixing and an enhancement of migration, Passioura (1971), Passioura and Rose (1971). Finally, dispersion may be caused by the instability of a displacing front. This may occur if significant viscosity or density differences occur between the displaced and displacing solutions, Nunge and Gill (1970). An analysis of its occurrence is given by Heller (1966). It results in the movement nonuniformly through the soil of the invading solution.

If we look at a real soil with a continuum of pore sizes, we might conclude that a soil of uniform small pores could optimize the attenuation of trace contaminants: uniform, to provide efficient mixing; and small, to maximize the surface area with which the solution comes in contact. However, in asking for small pores we minimize the rate a solution can be passed through the soil. In addition, the presence of unsaturated conditions may offset the effect of large pores.

The soil scientist has long recognized the great variability of pore size distribution in natural soils. This justifies the recommendation for mechanical treatment of the soil in preparing the land for disposal of solid waste leachates and liquid wastestreams. This requirement is not unusual nor impractical since soil manipulation is already a practice recognized in lagoon, artificial lake, and the more sophisticated sanitary-landfill operation. Use of the 'cell' system to surround (enshroud) solid waste on a daily basis is a required practice in well managed disposal sites. The soil encasing the waste thus is disturbed and

¹Ped--A unit of soil structure such as an aggregate, crumb, prism, block, or granule, formed by natural processes.

ends up in a more homogeneous mixture than the natural soil with respect to texture, structure, and pore size distribution. The "soil column" studies in the laboratory thus more closely resemble what should be expected in "prepared" disposal sites than that of the "natural" soil. Moreover, in the disposal of aqueous effluents from municipal sewage plants onto agricultural land, golf courses, etc., a certain layering or depth of disturbed soil will be encountered which is more homogeneous in physical characteristics than the original soil as a result of tilling, moving, spreading and other physical management.

Moisture Relationships--It has indirectly been implied from previous sections that water plays an important role in the attenuation and migration of trace contaminants. Here, the influence of the water status of the soil beneath a disposal site is emphasized. Unfortunately, in general, the soil moisture regime of any geographical area is not well defined. Smith (1973) has outlined the classification scheme used by the Soil Survey Staff. One alternative to this approach is to use climatic data as described by Scrivner et al. (1973) to estimate the moisture distribution. More reliable, however, would be the actual monitoring of the site. Without some estimate of how much, when, and where water moves through the soil, it will be difficult, if not impossible, to determine how solutes will migrate or attenuate.

The primary importance of moisture movement in the soil is simply as a medium of convective transfer of the trace contaminant. The net movement of solute depends on the relative magnitudes of the moisture flux and the rate of reaction. Only limited attempts have been made to model such systems for time-dependent and unsaturated use (Bresler and Hanks, 1969; Warrick et al., 1970; and Bresler, 1973-1974).

The secondary effects which unsaturated moisture conditions may have are varied. Biggar and Nielsen (1960) discuss the effect of diffusion and dispersion. They find that these effects are magnified as the column becomes unsaturated. Other effects can be discerned on the precipitation and dissolution of salts (Garrels and Christ, 1965), redox potentials (Bohn,

1971), biological reactions (McLaren and Skujins, 1968), and entrapped gases (Orlob and Radhakrishna, 1958). These effects may be involved and interrelated; they are not well understood, particularly in their net effect on the attenuation and migration of solutes.

Initial attempts at modeling this complex system will necessarily be crude. Several groups of researchers are looking at complex systems of reacting chemicals, but most assume instantaneous reaction as a basis for their analysis (Morel and Morgan, 1972; Dutt, 1962).

One point that has not been examined is the influence of solution flux on the attenuation or migration of trace contaminants. Fluctuating flow rates and dispersivity have been modeled by Warrick et al. (1972). Also from the work of Skopp and Warrick (1974) we would expect maximum attenuation at the lowest fluxes; however, the change in attenuation with flux is most dramatic at high fluxes. The influence of pore-size distribution and flux is presently being studied using a similar approach as given in Skopp and Warrick (1974).

Adsorption (Physico-chemical)--Chemical adsorption received earlier attention under chemical mechanisms but the more physico-chemical oriented mechanisms were not emphasized. Discussions of adsorption appearing in the literature often do not include a clear delineation between chemical and physical adsorption processes. Perhaps it is not too much to expect, because the mechanisms of adsorption are not well established. To illustrate, Murrmann and Koutz (1972) state that "Adsorption is the most important process by which chemicals are removed from wastewater applied to soil ... they are not well understood." The adsorption forces, which often dominate behavior of heavy metals in soils, particularly when the metals are present in the soil solution in small amounts, may be of various types. Only a small proportion of the reactions of heavy metals usually quantitized as adsorptive can be accounted for by chemical bonding. Solid state diffusion of specific ions (Cu and Zn) into octahedral positions in layer silicates may be possible if open crystal structure prevails, Banerjee et al. (1953), but Jenne (1968) believes this to be a minor mechanism of immobilization for

for most heavy metals.

Heavy metal adsorption most often has been related to sorption by the layer silicates which include (a) surface complex ion formation, (b) surface reactions, not ion exchange, (c) lattice penetration or inclusion, and (d) ion exchange. Other hypotheses concerning heavy metal adsorption include reactions with organic matter, lime, and hydrous oxides. There is enough information available now to broadly classify adsorption into four main groups:

1. Layer silicates
2. Hydrous oxides
3. Organic matter
4. Lime (carbonates)

Layer silicates--Solid-state diffusion known as "lattice penetration" is not a likely mechanism of consequence for heavy metals. Heavy metals appear to diffuse to a distance of a few atomic planes only at the crystal edges and along fractures. This is more of a fixation mechanism (i.e., retention against removal by salt solutions) than a sorption mechanism.

Layer silicates may bind soluble chemical species through two principal mechanisms, (a) ion exchange as the result of electrostatic attractions and (b) ion adsorption through covalent bonding. Ion exchange is relatively nonspecific and readily reversible, while ion adsorption may be very specific and at times irreversible. Ellis and Knezek (1972) have discussed mechanisms of Zn and Cu reactions with clay surfaces. Involved in these latter reactions are ion exchange (both with Zn^{++} and Cu^{++} ions as well as with the $ZnOH^+$ and $CuOH^+$ ions), precipitation of insoluble Zn and Cu salts, and some very specific covalent bonding between Zn, Cu, and the layer silicates.

Hydrous oxides--Jenne (1968) presents a good argument that sorption and fixation by the hydrous oxides in soil are the basic mechanisms for heavy metal immobilization. However, he also states, "the extent and rate

of reversibility of heavy metal sorption by the hydrous oxides, as well as the exact nature of the 'pH effect' on the reversibility is not entirely clear." The available data indicate that heavy metal adsorption by the hydrous oxides is at least partially competitive with and reversible to exchange with other heavy metals. Jenne (1968) further proposes that Fe and Mn supply the principal matrix into which less abundant heavy metals are adsorbed, coprecipitated, or occluded. In addition to the Fe and Mn hydrous oxides, Al hydroxides may play a role at times. Gibbsite ($\text{Al}(\text{OH})_3$) is a common mineral of our more heavily weathered soils and would undoubtedly play an important role in the mobility of some of the chemical species considered in this work (e.g., As forms very insoluble precipitates with Al). Also Al hydroxide polymers present on clay surfaces (of general occurrence in soil systems according to Jackson, 1963) may also play a role in immobilizing chemical elements in soil systems.

Organic matter--Reactions between heavy metals and organic matter are thought to involve (a) the formation of complexes, and (b) chelates. These are chemical reactions. Physico-chemical adsorption is often alluded to in the literature but not defined or quantitized. The extent to which organic matter plays a part in physico-chemical adsorption of the trace contaminants is not known.

Lime--Retention of trace and heavy metals by lime is more likely to be surface adsorption or surface precipitation by the carbonate ion. Jurinak and Bauer (1956) believe that zinc, for example, is adsorbed on the crystal surface of dolomite and magnesite at lattice sites that normally are occupied by magnesium. Later, Brown and Jurinak (1964) found that additions of CaCO_3 (lime) to Yolo fine sandy loam, beyond 5% (w/w), did not influence either Cu or Zn uptake by plants. The carbonate interaction was considered to be primarily a pH effect and secondly, an effect of carbonate-bicarbonate ion on heavy metal solubility.

Temperature Effect--The physical effects of temperature changes are minimal beyond 3 feet below the soil surface. On or near the surface,

freezing and thawing can directly cause insoluble or slowly soluble precipitates to form in the aqueous solutions. Trace and heavy metals will be carried out of solution with the organic matter and/or precipitate as salts of various crystalline and amorphous structures. Freezing is a concentrating and dehydrating mechanism. When freezing concentrates the solutes sufficiently to exceed solubility constants between constituents in the wastestreams and leachates, precipitation can occur. Freezing conceivably could be a very useful mechanism for natural control of trace and heavy metal in cold climates during the winter months. Re-solution of such precipitates upon thawing usually is slow, if at all. The process of freeze-drying or "salting-out" undesirable salts is an accepted process for purification of saline waters in western states. For further physical and chemical behavior of cationic concentration by freezing, see Malo and Baker (1973).

Temperature can also influence flow rates of water. There appears to be little data in the literature on the effect of temperature on flow rates involving wastestreams and leachates containing trace and heavy metals.

SECTION VI

SPECIFIC REACTIONS OF SELECTED HAZARDOUS CONSTITUENTS

The migration of selected elements, asbestos, and cyanide in soils is not known precisely and, because of the heterogeneity of field soils, it cannot be predicted from laboratory work with homogenized and repacked soils. Except for special cases where migration behavior is known because a specific waste has been applied to a particular soil, mobility in soil can usually only be inferred from a knowledge of the soil chemistry of the constituent in question and from a knowledge of the composition of the waste or leachate containing the constituent. As an aid in making predictions about migration and as background for other parts of the report, this section presents a selection of relevant information on specific chemical reactions of 10 elements, asbestos, and cyanide in pure systems and in soils. No attempt has been made to quantitize the reacting and resultant chemical species under specific conditions. Even if such information were available or could be constructed from a knowledge of the chemistry of the constituents, the information could not be applied practically because of the difficulty in measuring reaction conditions in the field. Some of the entries in this section are much larger than others because of the disproportionate amount of research attention that has been devoted to some constituents. It is hoped that the deficiencies of information will be remedied as more attention is focused on the chemistry and fate of wastes in soils.

ARSENIC

Unlike most of the potentially hazardous elements listed, arsenic has essentially no aqueous cationic chemistry and arsenate acts as a pH-dependent weak acid. Only trace amounts of arsenic appear naturally in soils. Arsenic has entered the soil in the past primarily through the use

of arsenical insect sprays and, to a limited extent, through disposal of some industrial wastes.

The most prominent mechanism of attenuation for arsenic applied to soils is adsorption by soil colloids (Murrmann and Koutz, 1972). Presant and Tupper (1966) studied the arsenic contents of six acid soil (Spodic) profiles by leaching them with dilute acid (0.1N HCl). They observed that under acidic soil conditions arsenic, on oxidation of the organic matter, migrates to the B and C horizons where it is probably associated with free iron and present in an adsorbed form. Jacobs, Syers, and Keeney (1970) showed that retention of As against extraction with NH_4Ac and Bray P-1 reagents from Wisconsin soils equilibrated with As (0, 80, 320 μg As/g added as NaHAsO_4) increased as the sesquioxide content increased. Also, as the free Fe_2O_3 content of the soils increased, the amount of As adsorbed from the solution increased. Amorphous Fe and Al compounds had a similar effect on As.

According to Tiffin, Lagerwerff, and Taylor (1973) As is known to associate with sesquioxides in a manner similar to iodine. A large fraction of As in soils is not extractable by citric acid. Although extractable by acids, the $(\text{Ca}(\text{As})_4)_2$ form is another rather immobile compound which frequently occurs in soil. Arsenate and arsenite usually appear in equilibrium (Misra and Tiwari, 1963). However, if poor drainage or waterlogging occurs, As appears in the reduced form which is more soluble and mobile than the oxidized form (Swaine and Mitchell, 1960). Upon the return of waterlogged soils to oxic conditions, arsenite becomes oxidized to arsenate through biological oxidation (Questel and Scholefield, 1953). These authors further state that the adsorption of arsenite at pH 7 is directly proportional to the amount applied and that small amounts of arsenite are irreversibly bound to soil. At the low concentrations usually found in waste waters, landfill leachates, and other aqueous wastestreams, As probably will not precipitate in soils except possibly as an impurity in phosphorus compounds formed over long periods of time.

ASBESTOS

Finely divided particles of asbestos are an air pollutant and a health hazard and cause lung cancer and a variety of other respiratory problems in human beings. Asbestos is a general term applied to certain minerals that form soft, flexible fibers in metamorphic rocks. The most common asbestos is chrysotile, a variety of the mineral serpentine, a magnesium silicate. Because of its fibrous, insoluble nature it has been used extensively in water filtration processes for clarification and purification. Because it is fireproof and flexible and has a fibrous nature, it is used extensively in fireproof clothing, blankets, heating coil insulation, and insulation placed around furnaces and heaters. It is also blown into attics and walls for insulation.

Asbestos is readily retained by the soil and deposits almost wholly on top of the soil regardless of the vehicle of transport. Colloidal particles $< 2\mu$ may penetrate the soil pores but not for any significant depth. Upon drying, asbestos again may be free for "pick up" by air turbulences unless incorporated into the soil.

Although there are no data on mobility of asbestos in soil, predictions about its behavior can be made with reasonable confidence. Since the weathering products of asbestos are the common nonhazardous salts of Ca, Mg, and Si, physical transport is the only mode of movement in soil which is of significance. The extensive data on movement of clay-sized ($< 2\mu$ diameter) particles by strictly physical processes provide a convenient yardstick for gaging the probable behavior of asbestos in soil. Clay particles 0.1 to 2.0μ in diameter are estimated to move at a rate of 1 to 10 cm per 3,000 to 40,000 years, depending on the soil texture (Berkland, 1974). There is no reason to expect that asbestos particles of similar sizes would move differently from this. Consequently, asbestos migration through soil will not be a problem of any significance.

Microorganisms and nonbiological geologic weathering will separate asbestos into its constituent, harmless parts; namely, calcium, magnesium, and silicate compounds, to join similar naturally occurring soil constituents.

Asbestos degradation, however, proceeds in soils at a very slow rate. Except as a possible dust hazard, asbestos does not offer a serious contamination prospect to the soil or underground water supplies and cannot be classed as a soil pollutant. Plowing or tilling the asbestos into the soil where it can be mixed in great dilution can control its chances of getting into the air as dust again. Surface waters can be polluted by asbestos which is washed into them. Consequently, precautions should be taken to prevent erosion from land disposal areas receiving asbestos.

Control of soil and water pollution from asbestos is straightforward and can be carried out with the technical knowledge which is now available.

BERYLLIUM

Commercial use of beryllium began about 1921. In the early 'forties, its use increased greatly to keep pace with an expanding air transport industry and in the late 'forties as part of the atomic energy development. Today, beryllium is used in many different manufactured products. It endows other metals with great strength, hardness, and resistance to corrosion. It is not capable of magnetization and is nonsparking. Precious gems, emerald and aquamarine, are varieties of beryl, $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$, which contain impurities (Beus, 1956). Chromium impurity yields emeralds, and FeO impart the blue to aquamarine.

Beryllium in certain chemical combinations presents a serious health hazard to those industrial workers susceptible to Be effects. It is particularly dangerous as an air pollutant.

In aqueous solution, only Be^{++} valence state occurs. Beryllium has the smallest radius ($r = 0.3\text{\AA}$) of the metal cations and a hydration number of 4. Hydroxides and fluorides complex Be^{++} in aqueous solutions and may be considered as the most important inorganic ligand in such solutions (Bondietti et al., 1973). Hydrolysis becomes detectable at about pH 3 in concentrations above 10^{-3} M. Precipitation of $\text{Be}(\text{OH})_2$ takes place with increasing pH when about one OH^- ion on the average becomes bound per Be^{++}

ion. Hydrolysis products are both monomeric and polymeric in solution. Baes and Mesmer (1973) emphasize the hydrolytic reactions of Be, in their review of trace contaminants, with these words:

"By far the most important hydrolysis product at beryllium concentrations about $10^{-3}M$ is the trimer $Be_3(OH)^{3+}$. Significant amounts of a dimer Be_2OH^{3+} are formed in the initial hydrolysis of more concentrated solutions. At least one other polymeric species, probably $Be_6(OH)_8^{4+}$, is formed in minor amounts in extensively hydrolyzed acidic solutions prior to the precipitation of the hydroxide.

"Because the polynuclear hydrolysis products of Be^{++} dominate at the usual metal concentrations studied ($> 10^{-3}M$), the mononuclear hydrolysis products $BeOH^+$, $Be(PH)_2$, and $Be(OH)_3^-$ can be examined by the usual equilibrium methods only at very low metal concentrations. The stability of $BeOH^+$ has been estimated by a kinetic method at ordinary concentrations while the stabilities of $Be(OH)_3^-$ have been estimated at very low beryllium concentrations from liquid-liquid extraction measurements and beryllium hydroxide solubility measurements, respectively. Estimates of the stability of these three monomeric species could be considerably improved by additional, more accurate measurements of the solubility of beryllium hydroxide. In strongly basic solutions ($> 0.1 M$) beryllium hydroxide dissolves to form the fully hydroxylated species $Be(OH)_4^{=}$."

Using ^7Be , Romney and Childress (1965) found that the isotope was strongly adsorbed by soils containing montmorillonite and illite-like clay minerals (Hanford and Vina soil) but not kaolinite. Furthermore Mg, Ba or Ca did not effectively replace ^7Be adsorbed to the two soils or bentonite even at high concentrations under "batch-equilibrium" conditions. These divalent cations, though, effectively competed with ^7Be for sorption sites in soil but not in bentonite suspensions. Magnesium, Ba, and Ca readily replace ^7Be from kaolinite.

Romney and Childress (1965) have this to report about their leaching column research:

"Additional tests on 300-g lots of Be-treated soil in leaching columns showed that virtually no Be was extracted from Hanford or Vina soil by 600 ml of distilled water and 0.1 M BaCl_2 , CaCl_2 , or MgCl_2 . Five successive leachings with 300 ml increments of 0.1 N HCl were required to extract significant amounts of Be from the treated soil. Equilibration-extraction tests showed that Be effectively displaced Ca, Mg, and Sr from sorption sites; Fe and P adsorbed by Hanford and Vina soil, however, were not influenced by Be treatments."

Beryllium reacts similarly to Al. It undergoes isomorphic substitution in the expanding lattice-type clay minerals as well as cation-exchange reactions. In summary, beryllium is strongly immobilized in soils, particularly those containing montmorillonite- and illite-like clays. It may displace divalent cations already on common adsorption sites in the exchange complex.

Evidence for Be organic attenuation or formation of soluble organic complexes in soil solution was not found in the literature at the time of this review.

CADMIUM

Adsorption on colloidal surfaces due to coulomb-type forces (Lagerwerff and Bower, 1972), is claimed to be primarily responsible for the immobility of cadmium in soils. Cadmium, like Zn, Hg, and Pb, undergoes hydrolysis at pH values encountered in soil environments, Hahne and Kroontje (1973). Cadmium belongs to the oxyphilic and sulfophilic group of elements. However, these elements (Zn, Hg, Pb, and Cd) must be treated differently since similarities in behavior do not extend to all reactions in soils. For example, Cd, Hg, Pb, and Zn demonstrate different hydrolysis species (Tables 6.1, 6.2 and 6.3). Compare the distribution of molecular and ionic species of divalent Cd, Hg, Pb, and Zn at different pH values in Figures 6.1, 6.2,

TABLE 6.1. THE FORMATION CONSTANTS AND SOLUBILITY PRODUCTS USED IN CALCULATIONS*

System	Formation Constants				Solubility Products	
	Log β_1	Log β_2	Log β_3	Log β_4	Precipitate	Log K_{sp}
Zn-Cl	0.43	0.61	0.53	0.20	Zn(PO ₄) ₂	-32.04
Cd-Cl	1.32	2.22	2.31	1.86	ZnS	-25.15
Hg-Cl	6.74	13.22	14.07	15.07	Zn(OH) ₂	-15.50
Pb-Cl	0.88	1.49	1.09	0.94	Cd ₃ (PO ₄) ₂	-32.60
Zn-OH	4.40	12.89	15.86	15.95	CdS	-27.92
Cd-OH	4.30	7.70	10.30	12.00	Cd(OH) ₂	-13.55
Hg-OH	11.86	22.13	--	--	Pb ₃ (PO ₄) ₂	-42.10
Pb-OH	7.82	10.88	13.94	16.30	PbS	-28.15
					Pb(OH) ₂	-19.52
					HgS	-53.50
					Hg(OH) ₂	-25.40
	Log β_1	Log β_{12}	Log β_{13}			
PO ₄ -H	12.325	19.532	21.693			
S-H	14.920	21.960	---			

*Adapted from Sillen and Martell (1971).

6.3, and 6.4. The very common and mobile chloride ion is a persistent complexing agent with Cd, Hg, Pb, and Zn (Table 6.4). The Cl⁻ concentration also differentiates these heavy metals markedly, depending on their affinity for such complex formations according to Hahne and Kroontje (1973).

Preliminary studies by Bondietti et al. (1973) indicate that the silt fraction of a Midwest soil, Dodge silt loam, immobilized ¹⁰⁹Cd as much as, if not more than, the sand and clay fraction. The greatest concentration of ¹⁰⁹Cd, though, was associated with the organic matter rather than inorganic mineral fraction of the soil. These same investigators state that "in soils and sediments the clay minerals, sesquioxides and the humic acids are the major components involved in adsorptive reactions." Carbonates are implicated in immobilization of Cd also but the mechanism is not clear.

TABLE 6.2. EFFECT OF CATION AND ANION HYDROLYSIS ON THE CONDITIONS SOLUBILITY AND SOLUBILITY PRODUCT AT THREE pH VALUES*

Precipitate	pH			
	4.0		8.0	
	S'/S	Log (K'sp/Ksp)	S'/S	Log (K'sp/Ksp)
Cation and Anion Hydrolysis				
ZnS	9.554×10^6	13.96	9.981×10^4	10.00
PbS	9.586×10^6	13.96	1.286×10^5	10.22
Cds	9.554×10^6	13.96	9.977×10^4	10.00
HgS	1.378×10^3	16.28	1.162×10^3	16.13
Anion Hydrolysis				
$Zn_3(PO_4)_2$	4.125×10^4	23.08	1.056×10^3	15.12
$Pb_3(PO_4)_2$	4.141×10^4	13.09	1.430×10^3	15.78
$Cd_3(PO_4)_2$	4.125×10^4	23.08	1.055×10^3	15.12
Anion Hydrolysis				
MS [#]	9.554×10^4	13.96	9.976×10^4	10.00
$M_3(PO_4)_2$	4.125×10^4	23.08	1.055×10^3	15.12
			3.038×10^3	6.97
			5.701×10	8.78

* From Hahne and Kroontje (1973).

@S' = conditional solubility derived from conditional solubility product K'sp; S = solubility derived from solubility product Ksp.

#M stands for Zn^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+}

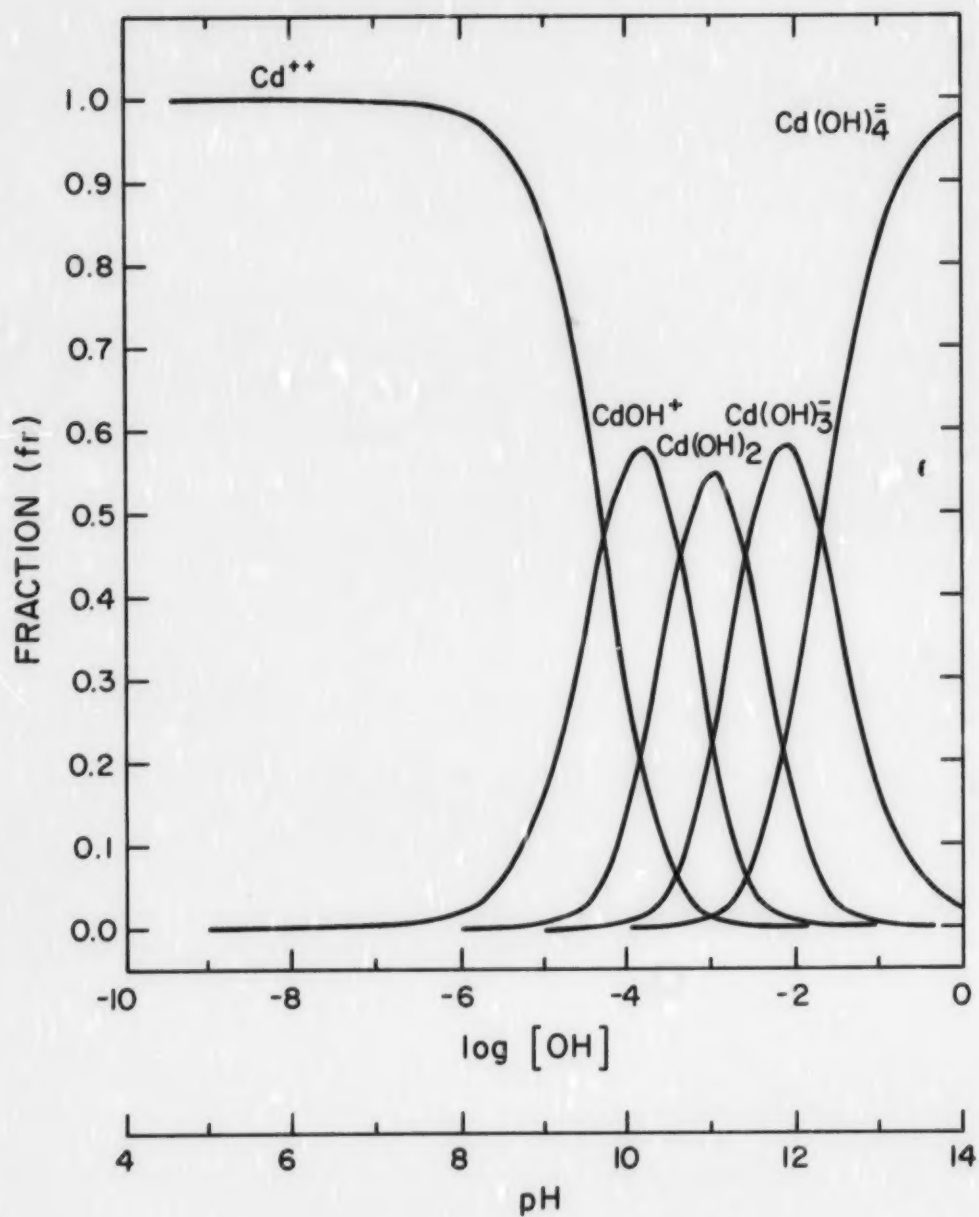


Figure 6.1. Distribution of molecular and ionic species of divalent Cd at different pH values (From Hahne and Kroontje, 1973).

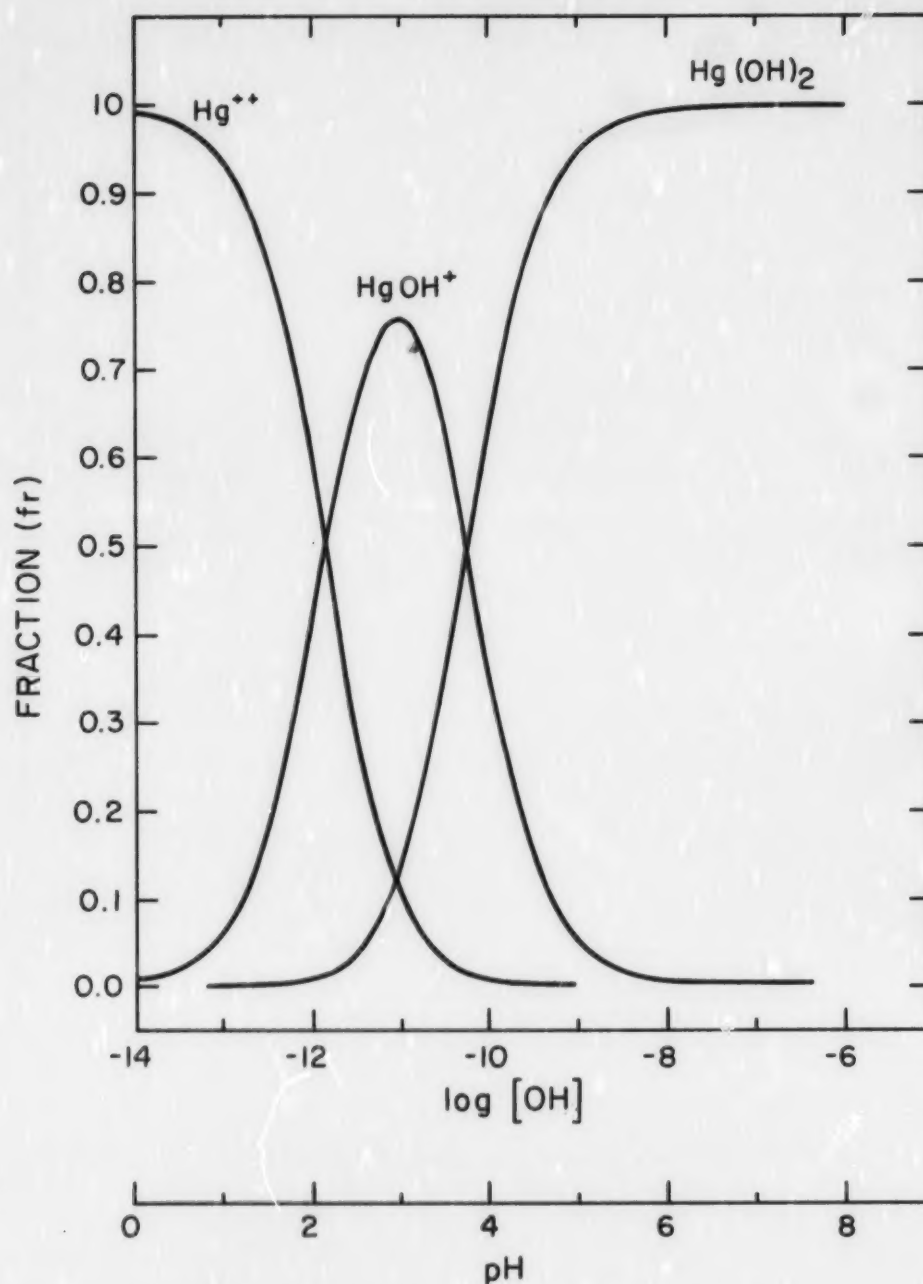


Figure 6.2. Distribution of molecular and ionic species of divalent Hg at different pH values. (From Hahne and Kroontje, 1973)

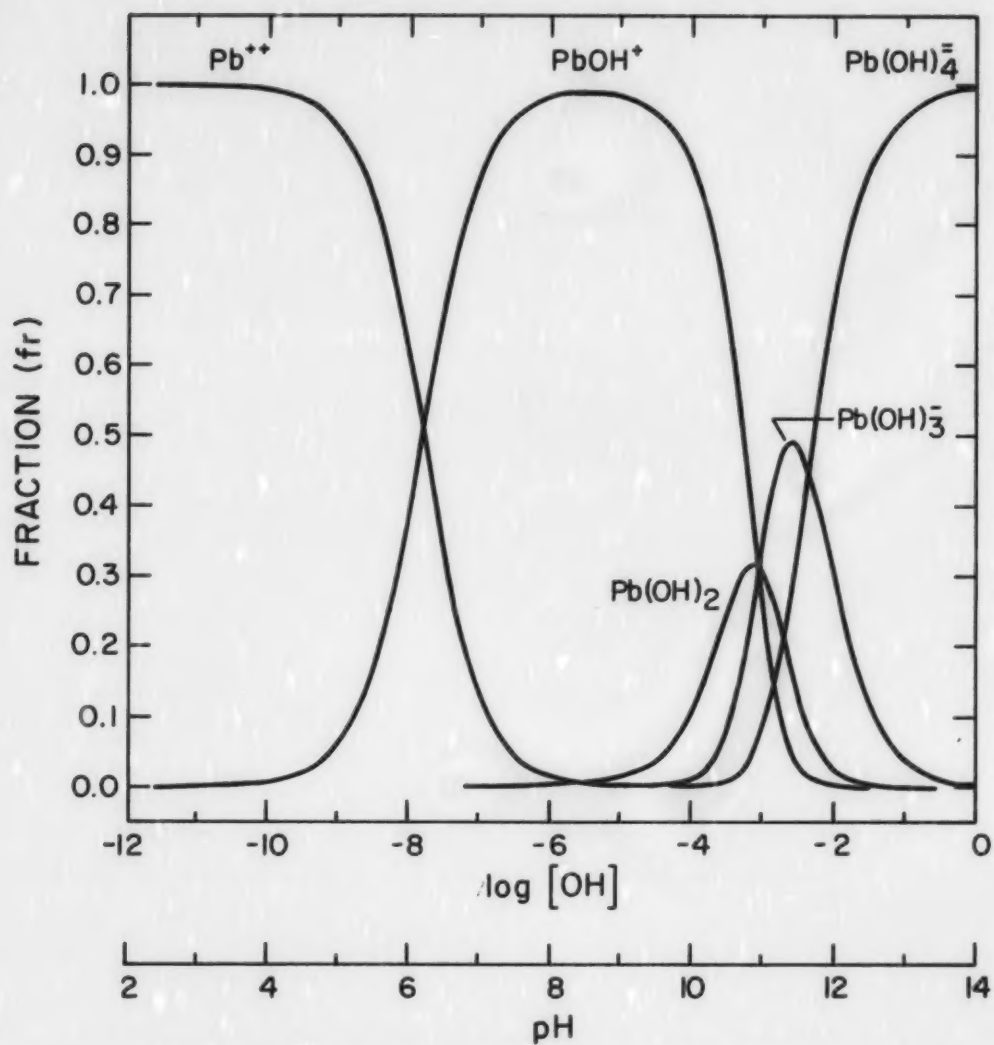


Figure 6.3. Distribution of molecular and ionic species of divalent Pb at different pH values. (From Hahne and Kroontje, 1973)

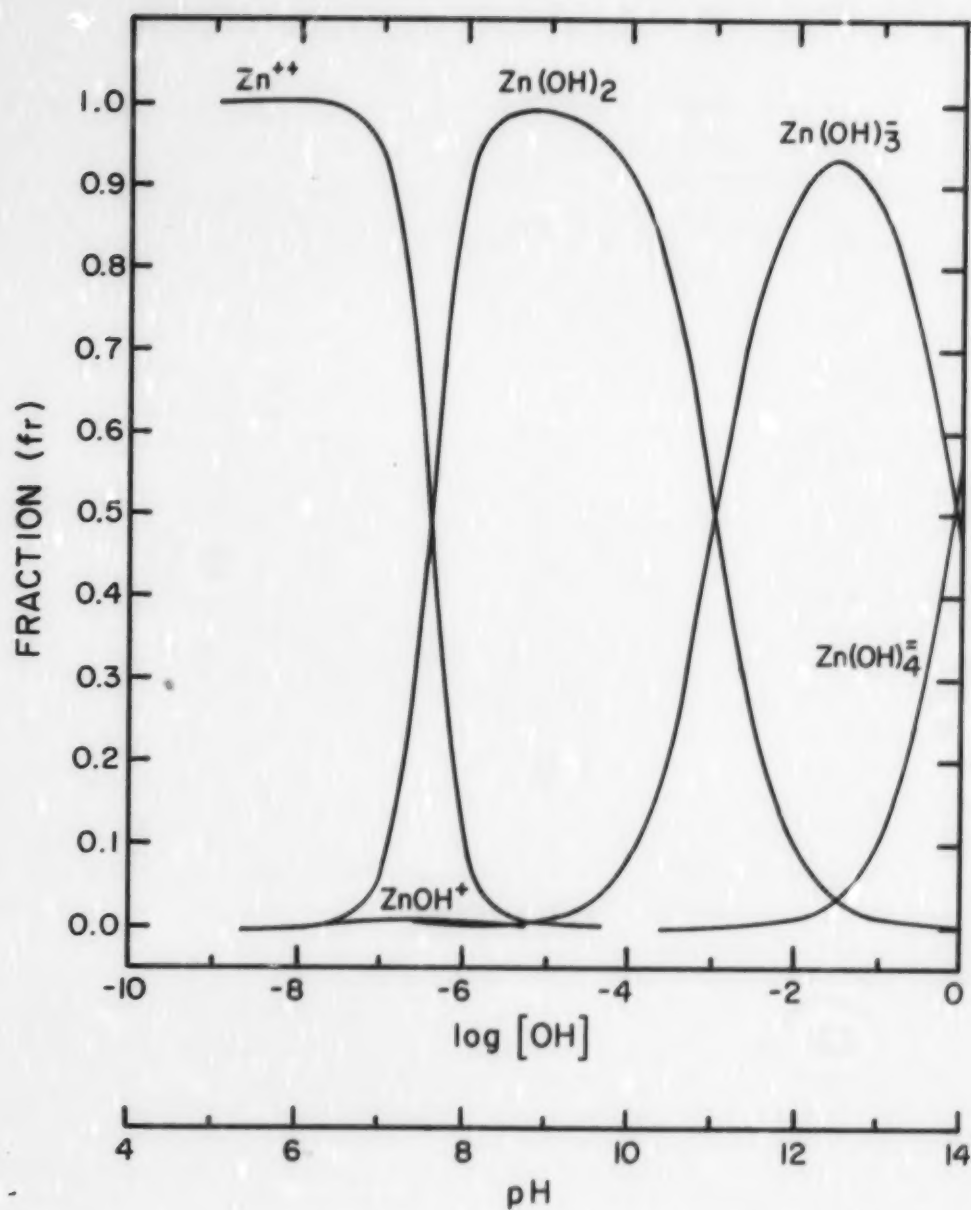


Figure 6.4. Distribution of molecular and ionic species of divalent Zn at different pH values (From Hahne and Kroontje, 1973).

TABLE 6.3. SOLUBILITIES AND INTRINSIC SOLUBILITIES OF Zn, Cd, Hg and Pb HYDROXIDES^{*a}

Component	Solubility moles/liters	(s) ppm	Intrinsic solubility moles/liter	S° ppm
Zn (OH) ₂	4.292 x 10 ⁻⁶	861 x 10 ⁻³	2.454 x 10 ⁻³	160
Cd (OH) ₂	1.917 x 10 ⁻⁵	384 x 10 ⁻³	1.412 x 10 ⁻⁶	150 x 10 ⁻³
Hg (OH) ₂	1.961 x 10 ⁻⁷	393 x 10 ⁻⁴	5.370 x 10 ⁻⁴	107
Pb (OH) ₂	2.151 x 10 ⁻⁹	431 x 10 ⁻⁶	2.291 x 10 ⁻⁹	474 x 10 ⁻⁶

* From Hahne and Kroontje (1973).

^aThe intrinsic solubility of the metal-ion hydroxides is defined as S° = [M(OH)₂] solution. Also, the metal-ion hydroxide concentration in solution can be expressed [(OH)₂] solution = B₂K_{sp} = S°.

The relative adsorption of Cd by selected minerals appears in Table 6.5 for comparative purposes. Literature on the hydrolytic behavior of Hg, Zn, Cd, Pb, Cu, and Be has been reviewed by Bondietti et al. (1973) in a report, Ecology and Analysis of Trace Contaminants, supported by the NSF-ORNL-EATC (June 1972-January 1973). Primary references for literature may be found compiled up to 1968 by Sillen and Martell (1971) under the title, "Stability Constants of Metal-Ion Complexes."

As contaminants from air, accumulation of Cd and Hg in soil is quite different. Cadmium adsorbs more to understory plants and litter than Hg (Baylock et al., 1973). Radiotracer techniques confirmed the expectation that Hg is more mobile in the Tennessee soils studied than Cd. Zinc, on the other hand, forms slightly more stable complexes with humic acids than Cd (Bondietti et al., 1973). These investigators compared Cd adsorption by humic acid and clays. The materials represented humic acid extracted from a local Captiva soil (Tennessee), a clay-organic fraction from Dodge silt loam, and a reference illite clay. The results of the Cd electrode titration curves for these materials using 50-mg samples in 100 ml of 0.1 M Ca(NO₃)₂ appear in Figure 6.5. Both the humic acid and clay-organo fraction

TABLE 6.4. EFFECT OF CHLORIDE CONCENTRATION ON THE CONDITIONAL SOLUBILITY AND SOLUBILITY PRODUCT

Precipitate	Chloride concentration					
	0.0001M		0.01M		1.00M	
	S'/S ^θ	Log (K'sp/Ksp)	S'/S	Log (K'sp/Ksp)	S'/S	Log (K'sp/Ksp)
Zn ₃ (PO ₄) ₂	1.000	0.00	1.016	0.004	4.604	3.32
ZnS	1.000	0.00	1.014	0.01	3.569	1.11
Zn(OH) ₂	1.000	0.00	1.009	0.01	2.336	1.11
Cd ₃ (PO ₄) ₂	1.001	0.01	1.130	0.27	39.83	8.00
CdS	1.001	0.00	1.017	0.09	21.55	2.67
Cd(OH) ₂	1.001	0.00	1.070	0.09	7.745	2.67
Pb ₃ (PO ₄) ₂	1.000	0.00	1.047	0.10	11.72	5.35
PbS	1.000	0.00	1.039	0.03	7.77	1.78
Pb(OH) ₂	1.000	0.00	1.026	0.03	3.926	1.78
HgS	4.082x10 ²	5.22	4.423x10 ⁴	9.25	3.619x10 ⁷	15.12
Hg(OH) ₂	5.503x10	5.22	1.214x10 ³	9.25	1.094x10 ⁵	15.12

* From Hahne and Kroontje (1973).

^θS' = solubility derived from conditional solubility product K'sp; S = solubility derived from solubility product Ksp.

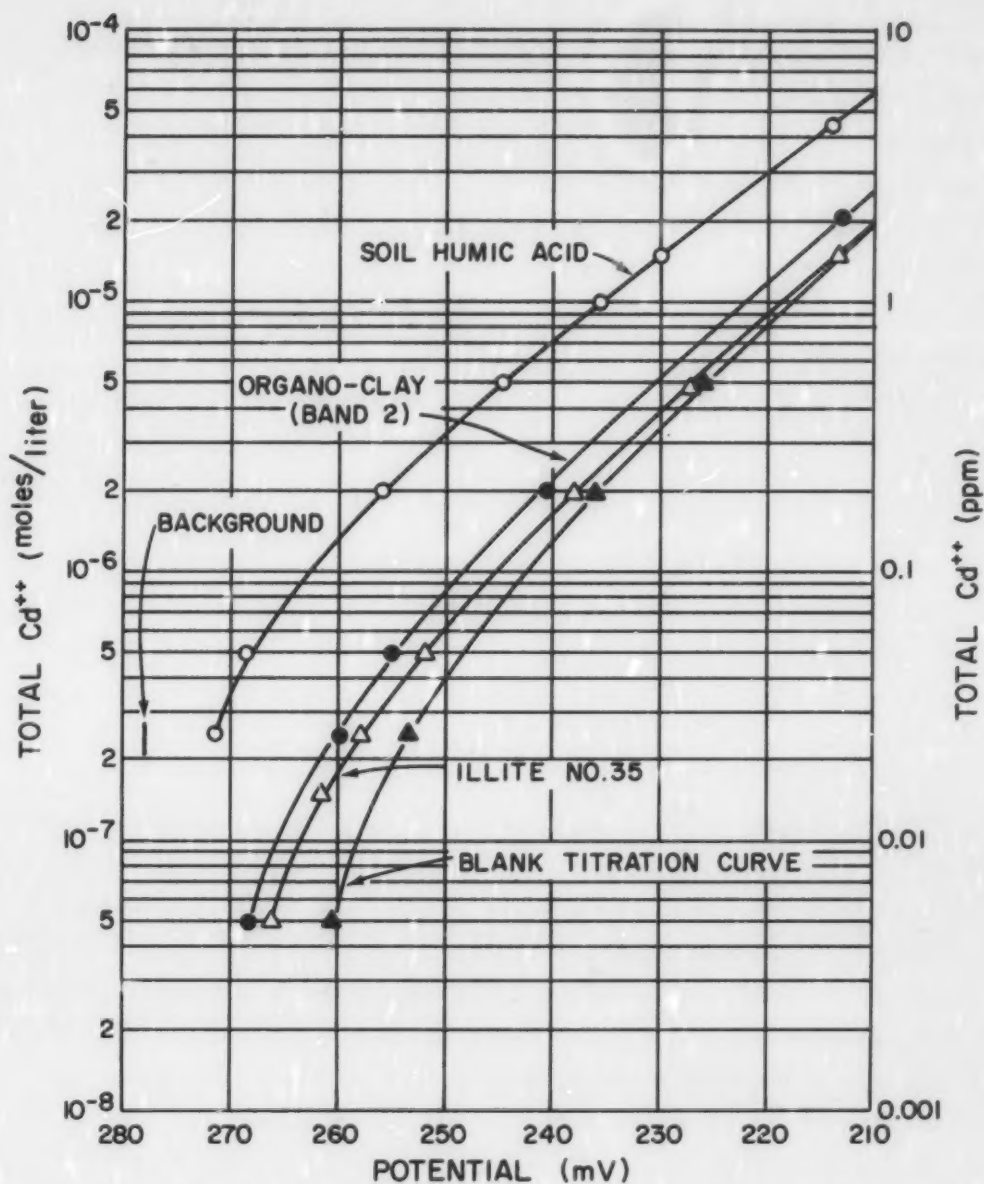


Figure 6.5. Cadmium electrode titration curves for soil humic acid, organo-clay, and illite. 50 mg samples in 100 ml of 0.1 M $\text{Ca}(\text{NO}_3)_2$. (From Bondietti et al., 1973)

TABLE 6.5. ADSORPTION OF CADMIUM BY SELECTED MINERALS*
(Solution was 0.025 M calcium acetate.)

Material	pH	K_d^{e}
Activated alumina powder	7.71	5642
Limonite (activated)	7.43	9578
Conasauga shale	7.59	2624
Fithian illite (< 2 μ)	7.60	1038
Muscovite (20-2 μ)	7.96	363
Biotite (20-2 μ)	7.90	220

* From Bondietti et al. (1973).

^e Fraction of cadmium adsorbed per gram divided by the fraction in solution (ml).

display high selectivity as well as high capacity for Cd adsorption. Illite is the poorest adsorber, though illite also demonstrates selective adsorption for Cd compared with such elements as Ca. From the data presented in Figure 6.6, Bondietti et al. (1973) draw this conclusion..."it should not be surprising that the mobility of cadmium in soils is very limited."

Before concluding the discussion on Cd, however, it seems desirable to return to Table 6.5. The distribution coefficient (K_d) shows that alumina and iron oxide have a higher adsorptive capacity than illite and far greater capacity than muscovite and biotite. These and other data (Figure 6.6) presented by Bondietti et al. (1973) make it quite evident that Cd has a selective adsorption affinity for oxides and/or hydroxyoxides of Fe and Al and strongly suggest that these constituents (often lumped under the heading of sesquioxides) are responsible for adsorbing most of the Cd applied to soils in aqueous wastestreams.

CHROMIUM

Chromium has two important oxidation states, trivalent and hexavalent. The latter is used widely in industries such as metal plating.

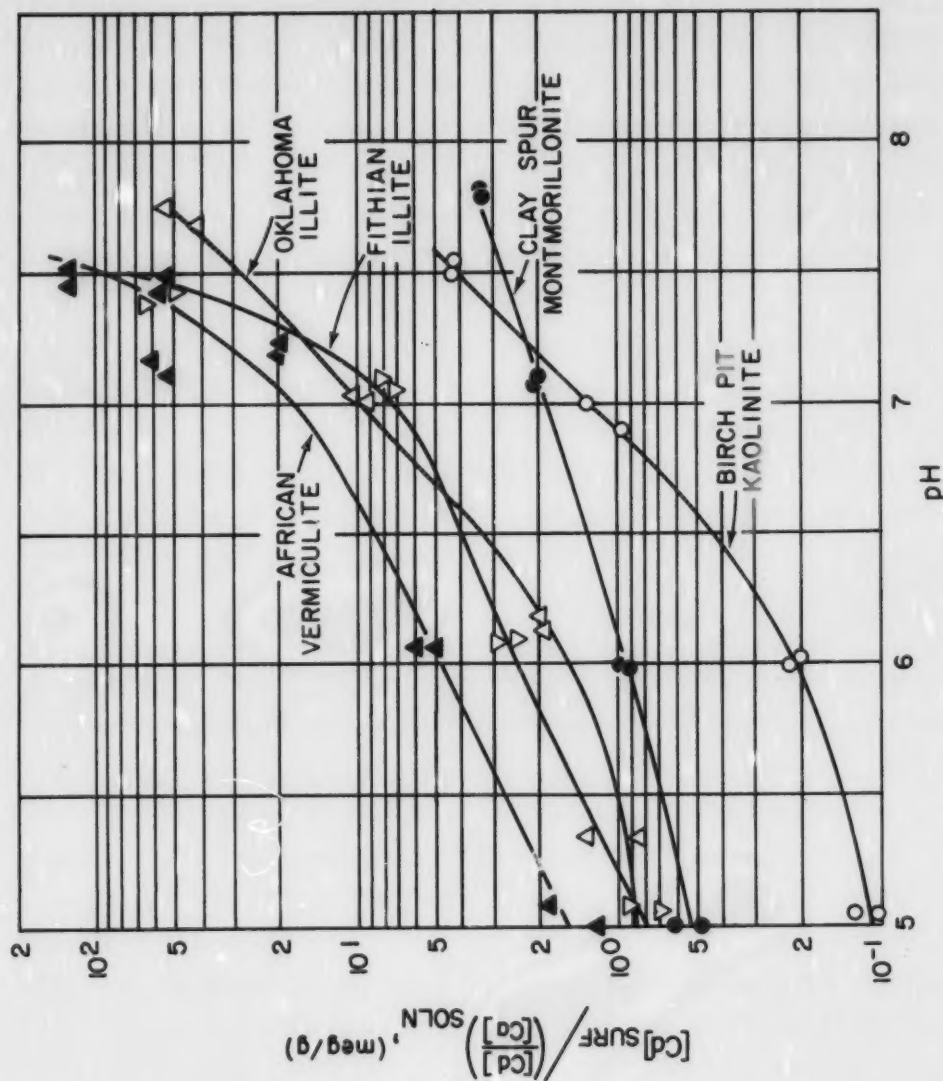


Figure 6.6. Relative adsorption capacities of clay minerals for low levels of cadmium in calcium solutions at 26°C. (From Bondietti et al., 1973)

Very little has been published about the chemistry of Cr in soils. The dominant species in soils is Chromium (III). Its concentration in the soil solution is limited by (a) adsorption on organic matter, clay minerals, Basu and Mukherjee (1964), and hydrous oxides of Fe, Mn and Al, and (b) precipitation as an oxide, and/or a mixture of the two.

Chromium (III) forms precipitates readily with hydroxides, carbonates, and sulfides, Murrmann and Koutz (1972). Although precipitation is probably not a major mechanism for Cr attenuation in soils at low concentration except at high pH values, it may well be an important immobilization reaction if aqueous wastestreams high in Cr enter the soil. In dilute solution the main mechanism is retention by adsorption at the surfaces of aluminum silicate minerals and iron oxides or hydrous oxides, Murrmann and Koutz (1972). The extent and rate of adsorption reactions probably will be determined largely by the type of adsorber present, the concentration of other ions in solution which would compete with chromium for exchange sites, and the pH. Reduction of solution concentration would be favored in soils with high contents of clay minerals and hydrous oxides of iron, aluminum, and manganese, and by a high pH (> 6.0). Precipitation reactions will likewise be favored by a higher pH.

Laboratory data published by Wentink and Edzel (1972) demonstrated that three different soils were capable of completely removing trivalent chromium from dilute solutions, and this suggests that percolation through soil may be an effective method of treating dilute chromium-bearing solutions. On the other hand, Deutsch (1969) reports instances of groundwater contamination by chromium (Cr^{+3} or Cr^{+6}) wherein the soil was not an effective treatment system, probably due to coarse-textured soil and high concentrations of chromium (both Cr^{+3} and Cr^{+6}) in the presence of high concentrations of other soluble salts.

The role of soil organic matter in controlling chromium concentration in solution is not well documented. Metals in general may be immobilized by adsorption as cations on the surface of lignin-like compounds, may be solubilized by complexing with organic acids and bases of low molecular

weight, and may form insoluble metal-organic precipitates. The extent to which these mechanisms apply to chromium chemistry in soils is not known although immobilization of Cr by exchange groups of organic matter may be expected to be fairly important. All of the heavy metals form soluble organic chelates with organic complexes in soil solution. Just how this balances out with adsorption is difficult to assess without further study.

At acidic pH values the hexavalent form of chromium is dichromate ($\text{Cr}_2\text{O}_7^{=}$), a powerful oxidizing agent (Tiffin et al., 1963). It would be expected, then, that hexavalent chromium applied to the soil would rapidly oxidize organic matter, leaving Cr (III). The conversion from hexavalent to trivalent will proceed more rapidly under acidic conditions. This may be a factor in the relation between soil pH and plant toxicity. In soils amended with hexavalent chromium, Patterson (1966) observed increasing toxicity with increases in soil pH.

The presence of Cr^{+6} in deep groundwaters of the desert Southwest, which frequently exceeds the U.S. Public Health acceptable drinking water quality limits, Dutt and McCreary (1970), might indicate a certain mobility of Cr not experienced by many of the other heavy metals. The relevance of this to attenuation of Cr by soils from "wastestreams" is not known.

The only important physical transport mechanisms in soils are downward movement in solution and erosion of solid material from the soil surface. Very little quantitative data on movement down through different types of soil (except as noted earlier) and on the extent of erosion transport are available, but some qualitative estimates can be made.

Other things being equal, downward transport will be more rapid in coarse-textured soils than in fine-textured soils because of the larger pores and therefore faster movement of the soil water, and smaller amounts of clay minerals. Similarly, transport through the soil will be faster in higher rainfall areas because of the potential for more water entering the soil (Tiffin et al., 1963). Transport in solution will be affected not only

by the amount and rate of flow of soil water but also by the previously discussed chemical mechanisms which control the concentration of chromium in the soil solution.

For soils where added chromium remains near the surface because chemical mechanisms limit the concentration in soil solution, there is the possibility that soil particles with adsorbed chromium or precipitates of chromium will be eroded from the surface by irrigation and/or rainfall and carried into surface waters (Tiffin et al., 1963). This would be particularly significant and should be considered when designing disposal sites for sewage or industrial sludges where the soil has been selected or treated to maximize heavy metal retention in the surface.

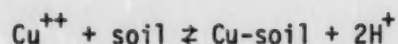
COPPER

The important oxidation state of Cu in soils is +2. In the presence of organic acids, organic-complex - COOH groups, -OH groups, etc., in landfill leachates, Cu^+ may be present. Cupric ion hydrolyzes to a slight extent prior to precipitation (Baes and Mesmer, 1973). $\text{Cu}_2(\text{OH})_2^{++}$ is the only polymeric species whose identity is well established. Investigators do not agree on the stability of $\text{Cu}(\text{OH})^+$, though there is evidence supporting interpretation in terms of $\text{Cu}(\text{OH})^+$ and $\text{Cu}_2(\text{OH})_2^{++}$ in acidic solutions.

Schindler et al. (1965), who studied the stable phase of CuO at 25°C relative to surface area on the solubility of CuO, found that the only basic species appears to be $\text{Cu}(\text{OH})_4^{=}$. The mononuclear species, $\text{Cu}(\text{OH})_2(\text{aq})$ and $\text{Cu}(\text{OH})_3^-$, are not well established so the minimum solubility of the oxide is still virtually unknown.

The carbonate complexes of Cu have very high stability constants (Schindler et al., 1968). Carbonates $\text{CuCO}_3(\text{aq})$ and $\text{Cu}(\text{CO}_3)_2^{=}$, occur readily. Schindler (1968), who further defined the $\text{Cu}^{++}\text{-CO}_2\text{-H}_2\text{O}$ system, shows the solid state to be $\text{Cu}_2(\text{OH})_2(\text{CO}_3)$ malachite and $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ azurite.

Lindsay (1972a) has prepared a diagram of the solubilities of various Cu minerals (Figure 6.7) showing the Cu-soil curve which is represented by the reaction



The log K value as developed in five soils by Norvell and Lindsay (1969) was found to be - 3.2 expressed by the equation:

$$\text{Cu}^{++} = 10^{3.2}(\text{H}^{+})^2.$$

This equation gives the approximate concentration of Cu^{++} maintained in soils. According to Figure 6.7 the Cu-soil level falls considerably below that of the individual Cu compounds. Lindsay (1972a) also prepared another diagram, Figure 6.8, to show the relationship among soluble Cu species expected in soil solution in equilibrium with the Cu-soil complex defined in the above equations. The diagram shows that below pH 7.3, Cu^{++} predominates while above this, CuOH^{+} is most prevalent. $\text{Cu}_2(\text{OH})_2^{++}$ and $\text{Cu}(\text{OH})_3^{-}$ are less abundant and $\text{Cu}(\text{OH})_4^{-}$ falls outside the diagram.

Again, the movement of cuprous or reduced forms of Cu through soil, as may be expected below landfills producing leachates is not documented in the literature. The present soils information is limited to the oxidized form. The research of Cu attenuation by soil organic matter, for example, is fairly extensive. The general consensus is that Cu is strongly complexed to organic matter, Hodgson, Lindsay, and Trierweiler (1966).

Jenne (1968) proposed that the hydrous oxides of Mn and Fe provide the main control on the immobilization of Cu as well as Co, Ni, and Zn in soils and fresh water sediments. The hydrous oxide furnishes the principal matrix in soils into which Cu and Zn (heavy metals) may be adsorbed, coprecipitated, and occluded. All of these reactions contribute to attenuation of Cu.

Gilbert (1952) and Lucas (1948) report that leaching of copper in agricultural soils is negligible.

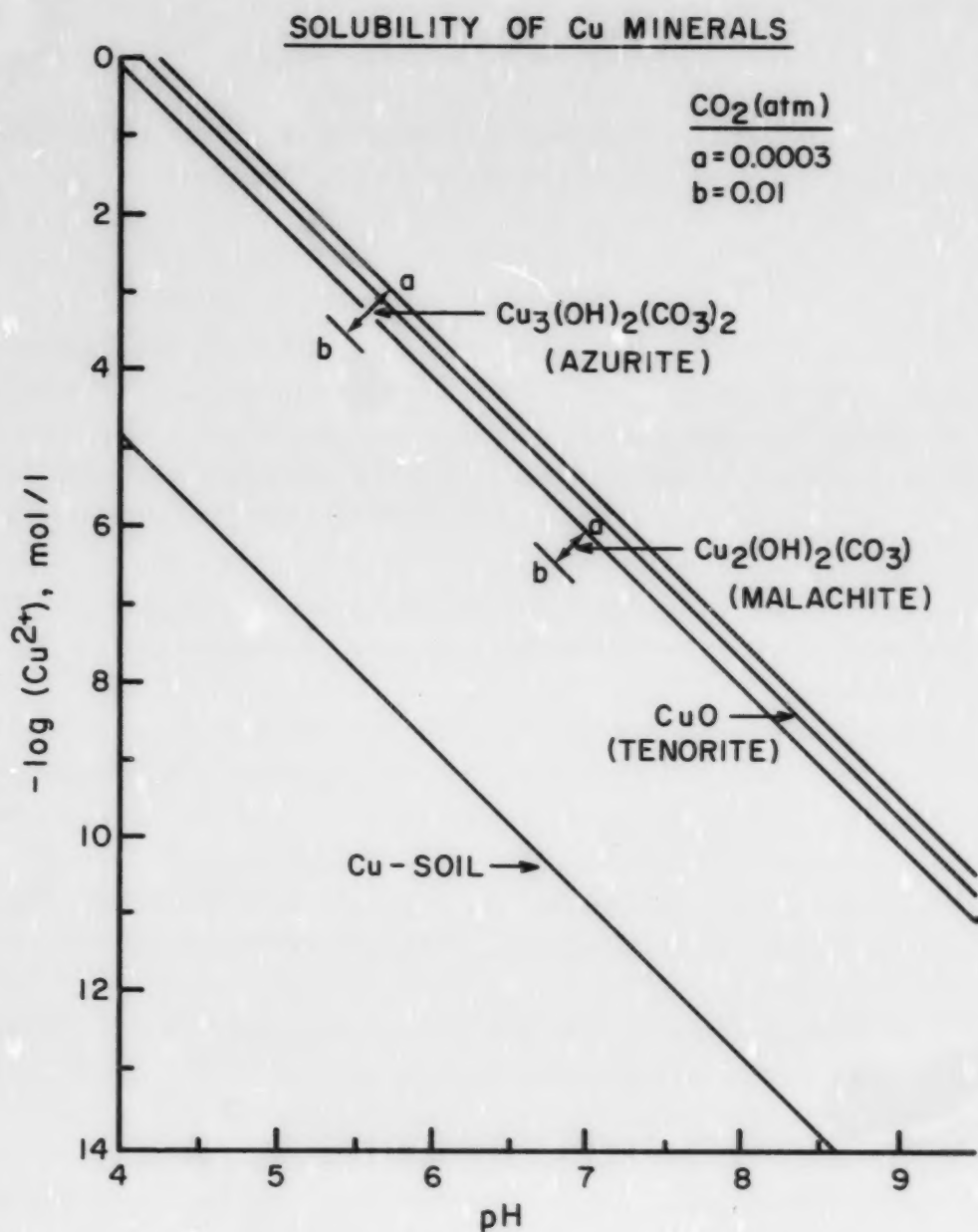


Figure 6.7. The solubility of various Cu minerals compared to that of soil Cu.
 (From Lindsay, 1972)

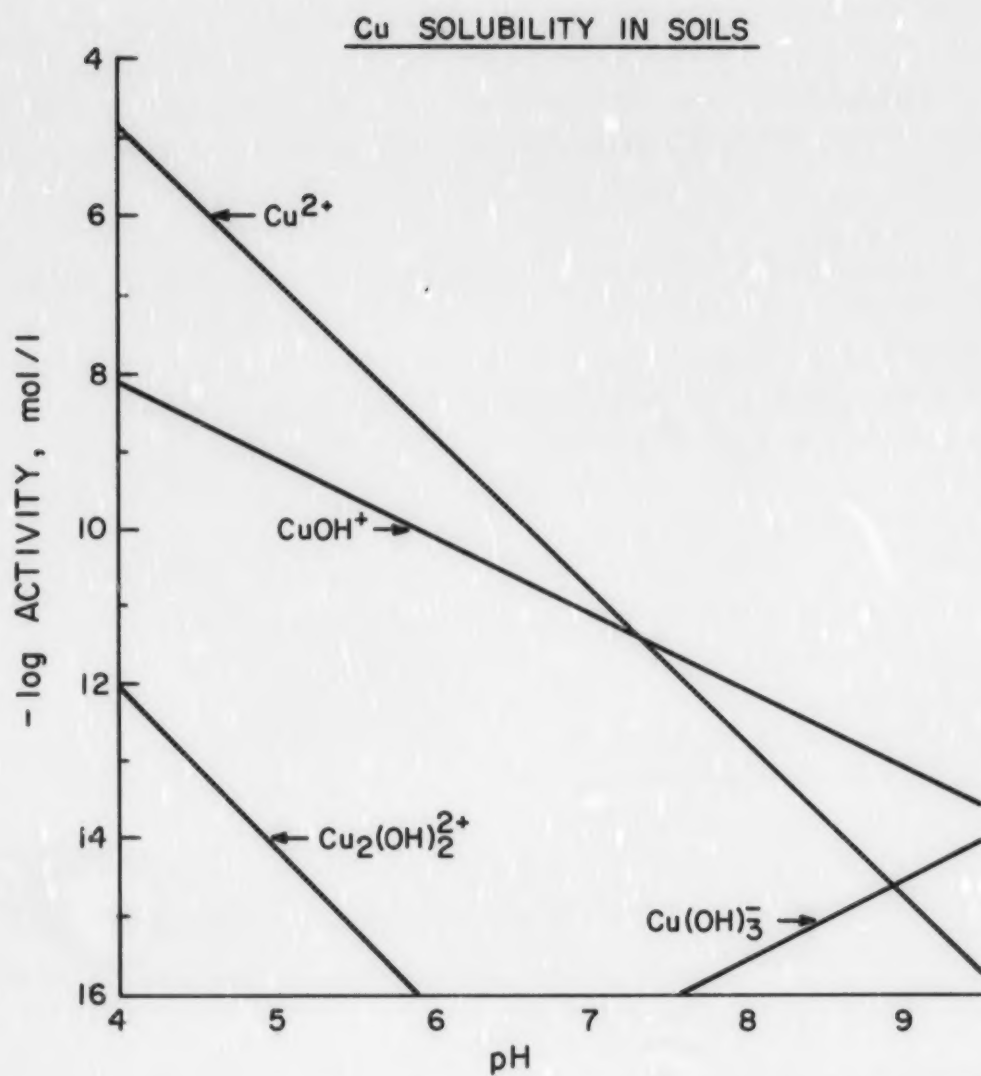


Figure 6.8. Soluble Cu species in solution equilibrium with soil Cu.
(From Lindsay, 1972)

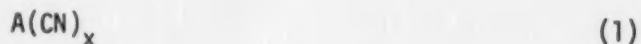
CYANIDE

Cyanides are found in effluents from coal-burning furnaces, gas works, and coke ovens, from the scrubbing gases of steel plants, from metal cleaning and electroplating processes, and certain chemical industries.

Cyanide is an anion (CN^-) and, as such, is not strongly retained in soils. Except for AgCN , cations form at least slightly soluble salts with CN^- .

Cyanide appears in nature and industry in so many chemical and biological combinations and forms, it requires immediate strict definition in order that this discussion may move forward in as clear a manner as possible. In industrial wastes, "cyanide" refers to all CN groups in the cyanide compounds present that can be determined as the cyanide ion, CN^- , by the methods used, Taras (1971). The cyanides are further conveniently classified into (a) simple and (b) complex groups.

The simple forms occur as

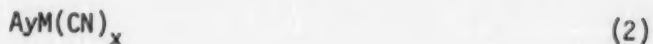


where A = an alkali (Na, K, NH_4) or a metal

x = the valence of A and the number of CN groups

and CN = is present as CN^-

The complex forms are many and varied but the alkali-metallic cyanides have the formula:



where A = the alkali present y times

M = a heavy metal (Fe^{++} , Fe^{+++} , Au, Cd, Cu, Ni, Ag, Zn and others)

x = the number of CN^- groups and equal to the valence of A taken y times plus that of the heavy metal.

The anion radicals in the complex cyanides appear as $\text{M}(\text{CN})_x^-$.

When the simple cyanides come in contact with acids, HCN forms. The metal cyanides vary widely in their decomposition to HCN in acid. As a matter of convenience they may be grouped further, on a basis of rate of decomposition, as readily decomposable (metallic forms of Ag, Au, Cd, Cu, Ni, Pt, and Zn) and slowly decomposable (Fe and Co).

The stability of alkali-metallic cyanides also vary in aqueous solution alone. Many remain rather stable in water. Because of the toxicity of CN^- , the formation of the more stable cyanides has been a significant factor in the activity of biological systems.

Cyanide in Aqueous Wastestreams

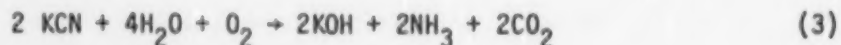
Studies involving cyanides and aqueous wastestreams, although only indirectly related to cyanide attenuation in soils, provide some clues to chemical and biological reactions which may be expected to occur in soils. Reactions in most wastewaters (landfill leachates, sewage waters, polluted streams, and wastewaters from a wide variety of industrial sources) are more readily definable in aqueous than soil media. Moreover, toxic limits of CN to biological systems appear to be more readily identified in the absence of the great sorption and buffering variables of soil materials. The identification and evaluation of CN^- in sewage, leachate, waste, and polluted waters appears, from our studies at Arizona, to be much more quantitative than for soils. A number of procedures have been reviewed by Taras (1971), certain of which are offered as quantitative with the exception of cobaltcyanide. Sulfides, heavy-metal ions, fatty acids, oxidizing agents, and other interfering substances which often respond to removal by distillation, however, can seriously influence the qualitative evaluation of CN. These may be expected to be some of the same substances which influence the migration rate of CN in soils.

Virtually no organic compound is left immune to degradation by the highly versatile microbial population. Cyanide is no exception despite the fact that it is highly toxic to biological systems as CN^- (Taras, 1971; Ludzack et al., 1951; and Dodge and Reams, 1949). Simple alkali cyanides

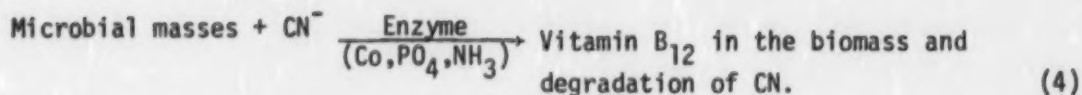
and many alkali-metallic cyanides, which form CN^- in aqueous solution, may decompose slowly to form varying degrees of toxicity. The level of toxicity of the more stable cyanides depends on the metal present and the proportion of CN groups converted into simpler alkali cyanides.

The threshold limit of CN^- toxicity on biological activity of aqueous systems also varies widely with such environmental factors as water quality, temperature, type, and size of the organism. Thus, definite effects cannot be established except in terms of the nature of the effects. For example, Lockett and Griffith (1947) report that 5.0 ppm of CN in sewage treated by the activated process had a marked depressive effect on the purification process, whereas Ludzack et al. (1951) found inhibitory effects as low as 0.3 ppm under certain other conditions. In concentrations of 6% CN, all waters studied were purified up to 50% or more of the control within 10 days of incubation.

Of particular interest because of its toxicity to the cytochrome system is the utilization of cyanide by specific microorganisms. Ware and Painter (1955) isolated an aerobic autotrophic actinomycete contained in sewage which is capable of growing on silica gel containing only KCN as a source of carbon and nitrogen. This organism can utilize concentrations of CN up to 15 mgm/100 ml but grows more favorably at 4 mgm/100 ml concentrations. The rate of utilization in colony culture approached a maximum of 0.5 mgm CN/day. Presumably the general reaction proceeds as follows:



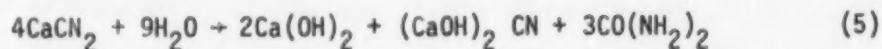
Other examples of specific microbial assimilation and transformation of CN in synthetic media (not soil) are those of Reynolds (1924), and Strobel (1964). All the active organisms are fungi. Howe and Howe (1966) patented a process for biological degradation of CN using the biological masses of the activated sludge system. They claim to have successfully degraded or detoxified more than 570,000 lb of CN^- in a year. The system does not require any specific organism and may be written as:



Cyanide in Soils

Cyanide finds its way into soils primarily through the activity of man, although it is actually produced by some fungi (Bach, 1956), at least one bacterium (Michaels and Corpe, 1965) and many higher members of the plant kingdom (Robinson, 1962). Cyanide also is utilized as an energy source and/or source of nitrogen by plants and microorganisms (Goldschmidt and Butler, 1963; Allen and Strobel, 1966; and Ware and Painter, 1955). In fact, cyanide and such related compounds as cyanamide, dicyanodiamide, and guanidine nitrate have long been regarded by agriculturalists as potential nitrogen fertilizers. As early as 1918 Cowie (1919) of the Rothamsted Experiment Station, Harpenden, England, recognized that cyanamide can serve as a valuable fertilizer because it forms ammonia readily in soils. Nitrate-nitrogen then accumulates through the usual microbial-ammonia-oxidation channel (Cowie, 1919; McCool, 1945; and Fuller et al., 1950a, 1950b).

Fuller et al. (1950), using a calcareous soil and Volk (1950), using an acid soil, found that cyanamide was inhibitory to ammonia nitrification in soil at high concentrations. In the calcareous soil cyanamide was readily converted to nitrate when applied at a rate of 100 ppm N. At a rate of 200 ppm N only about half of the nitrogen was converted to ammonium-nitrogen during the year, and only small amounts of nitrate-nitrogen were detected. The pH at the high rate was 8.0 or above. At pH values below 7 the reaction probably is:



See Fuller et al. (1950). The urea may then hydrolyze to yield $\text{NH}_3 + \text{CO}_2$.

At pH values between 7 and 8 both reactions may be expected to occur with the formation of urea exceeding that of dicyanodiamide.

Anaerobic soil conditions presumably cause cyanamide to decompose, yielding nitrogen gas.

Dicyanodiamide applied to a calcareous soil was found by Fuller et al. (1950a) to yield only small amounts of ammonium-nitrogen over a year's time. Nitrates did not form in appreciable quantities and were depressed even below that of untreated soil. Cowie (1919) also claimed dicyanodiamide gave no evidence of nitrification in soil over periods of several months. Dicyanodiamide inhibits oxidation of ammonia, although it may not be toxic to organisms other than the nitrifiers.

Cyanide (CN^-) added to soil in modest amounts (up to 200 ppm NaCN) appears to be readily transformed and/or degraded depending on the oxidation/reduction conditions. In fact, McCool (1945) suggests it is only slightly less effective as an N-fertilizer for tobacco, corn and mustard than sodium nitrate when applied to nitrogen-deficient, acidic soils. Cyanide as KCN^{15} was shown by Strobel (1967) to yield CO_2 and NH_3 in non-sterile soils. He further suggests that cyanide is fixed by various soil organisms in several ways, all of which give rise to some organic nitrile. The nitriles yield ammonia plus the corresponding organic acid as a result of nitrilase activity. Many microorganisms of the soil can utilize ammonia and "fix" the N in the form of living cells. Strobel's (1967) experiments with doubly lab labeled CN ($\text{C}^{14}\text{N}^{15}$) showed that the N of the cyanide was retained more firmly than the C. Mobility of CN^- through soil according to McCool also appeared to be slower than that of nitrate from sodium nitrate sources.

Despite the fair amount of information on cyanide reactions in natural and waste systems, a number of critical gaps exist which need filling before predictions concerning the fate of CN^- under such a wide variety of habitats as the soil can be made with confidence. Some of the most obvious deficiencies in information are in the area of anaerobic reactions. Since many of the CN wastestreams, waste ponds, and leachates end in an anoxic anaerobic habitat, a research program to obtain data in this area was initiated.

Since data concerning the movement of cyanide in different soils are very limited and fragmentary, further study is needed. In particular, more information on rates of cyanide to harmless N_2 gas under anaerobic conditions is needed, since conditions are expected to be predominantly anaerobic at the leachate-soil junction under a landfill. Analytical procedures for -CN in a mixed matrix such as soil are unusually difficult and time consuming to carry out.

IRON

Iron is universal. Soils contain large amounts of iron as compared to other trace and heavy metals. The clay minerals (aluminum silicates), sulfides, sulfates, oxides, and hydroxides all react to form compounds or complexes with iron. Under oxic conditions iron is present in solution as Fe^{3+} . Iron first forms the hydroxide and then proceeds to the insoluble Fe_2O_3 oxide forms on aging. Iron solubility and therefore mobility in soil is dependent both on pH and redox potential.

According to Jenne (1968):

"When $[(Fe^{3+})(OH^-)^3]_{soln}$ is greater than the solubility product, iron precipitates, presumably as $Fe(OH)_3(a)$, as a coating on clay surfaces. Discrete iron hydroxide particles appear to form only after a certain quantity of iron has been precipitated as a coating on the clay surface, Berg (1960) and Fripiat and Gastuche (1952). Attempts have been made to relate this phenomenon to the cation exchange capacity of the clay. For example, Fripiat and Gastuche (1952) found that the amount of iron oxide occurring as coatings on kaolinite was ten times the cation exchange capacity. However, Berg (1960) demonstrated that the amount of iron precipitated as coatings, before discrete oxide particles appeared, was about one weight % and eight weight % iron for the 2 to 0.2μ kaolinite size fractions, respectively; hence, the amount precipitated as coatings was related to the surface area of the clay rather than to cation exchange capacity. Fripiat and Gastuche (1952) observed that hydrogen (aluminum?) saturation of the kaolinite led to a definitely

amorphous iron oxide precipitate such that iron oxide continued to precipitate on the surface, whereas alkali or alkaline earth cation saturation of the clay led to a compact, nonporous coating which resulted in the latter portions of the iron precipitate forming discrete particles. In addition to iron precipitation on clay surfaces, colloidal iron hydroxide is readily sorbed onto clay-mineral surfaces, Follett (1965) and Fripiat and Gastuche (1952)."

Jenne also presents two diagrams of Eh and pH effects on the occurrence of iron minerals under equilibrium conditions (Figures 6.9 and 6.10). These lines are constructed by deriving equations, using Eh and pH, and relating adjacent phases. The Eh-pH values at which the two phases are in equilibrium are represented by the lines between the various phases. The dotted area in Figures 6.9 and 6.10 represents the range of conditions to which soils are exposed. The anoxic conditions most likely to occur in soils under landfills would fall on the dotted area at pH 0 to 4 or Eh 0 to -250 (mv). Eh values of the soil columns receiving leachate under anoxic or partially anoxic conditions in the University of Arizona study reach levels as low as -0 mv.

Because of the possible shift between Fe^{3+} and Fe^{2+} in aqueous wastes and in landfill leachates, the two equilibrium diagrams of Lindsay (1972a) are reproduced as Figures 6.11 and 6.12. Figure 6.11 illustrates the relationship between Fe^{3+} and Fe^{2+} in equilibrium with hydrous Fe (III) oxides and given O_2 partial pressure using the equation:

		<u>Log K o</u>
$\text{Fe}(\text{OH})_3(\text{s})$	$\text{Fe}^{3+} + 3\text{OH}^-$	- 39.40
$\text{Fe}^{3+} + \text{e}^-$	Fe^{2+}	13.02
$3\text{H}^+ + 3\text{OH}^-$	$3\text{H}_2\text{O}$	42.00
$\frac{1}{4}\text{H}_2\text{O}$	$\text{e}^- + \text{H}^+ + \frac{1}{4}\text{O}_2(\text{g})$	- 20.77
$\text{Fe}(\text{OH})_2(\text{s}) + 2\text{H}^+$	$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2(\text{g}) + 2\frac{1}{2}\text{H}_2\text{O}$	- 5.15

In Figure 6.12 the instability of some common Fe (II) minerals in relation to some hydrous Fe (III) oxides in soils is illustrated. Also

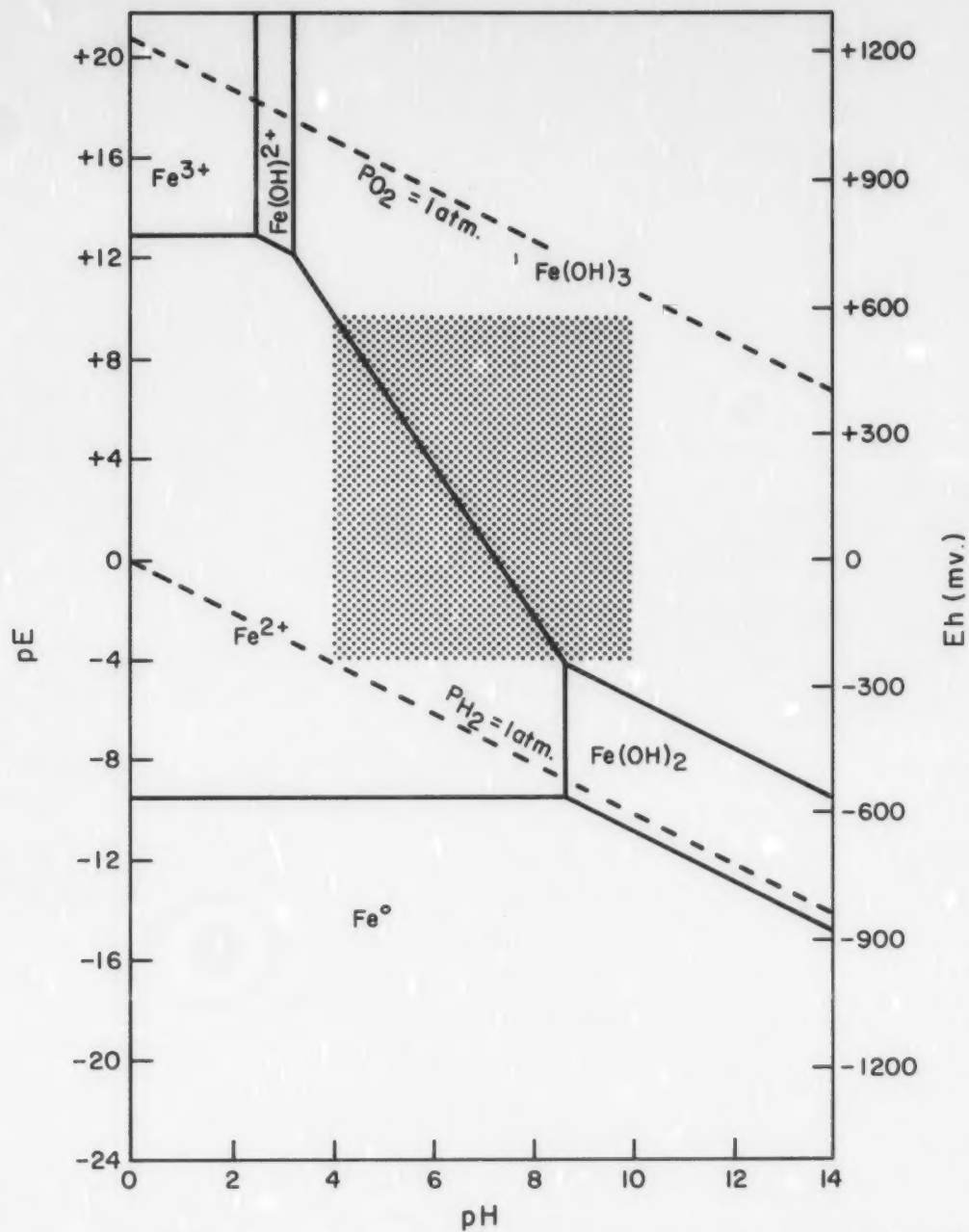


Figure 6.9. Eh (pE) vs. pH stability field diagram from iron ($a_{\text{Fe}} = 10^{-4} \text{M}$; $P_{\text{CO}_2} = 0$; $P_{\text{tot}} = 1 \text{ atm}$; $T = 25^\circ\text{C}$). (From Jenne, 1968)

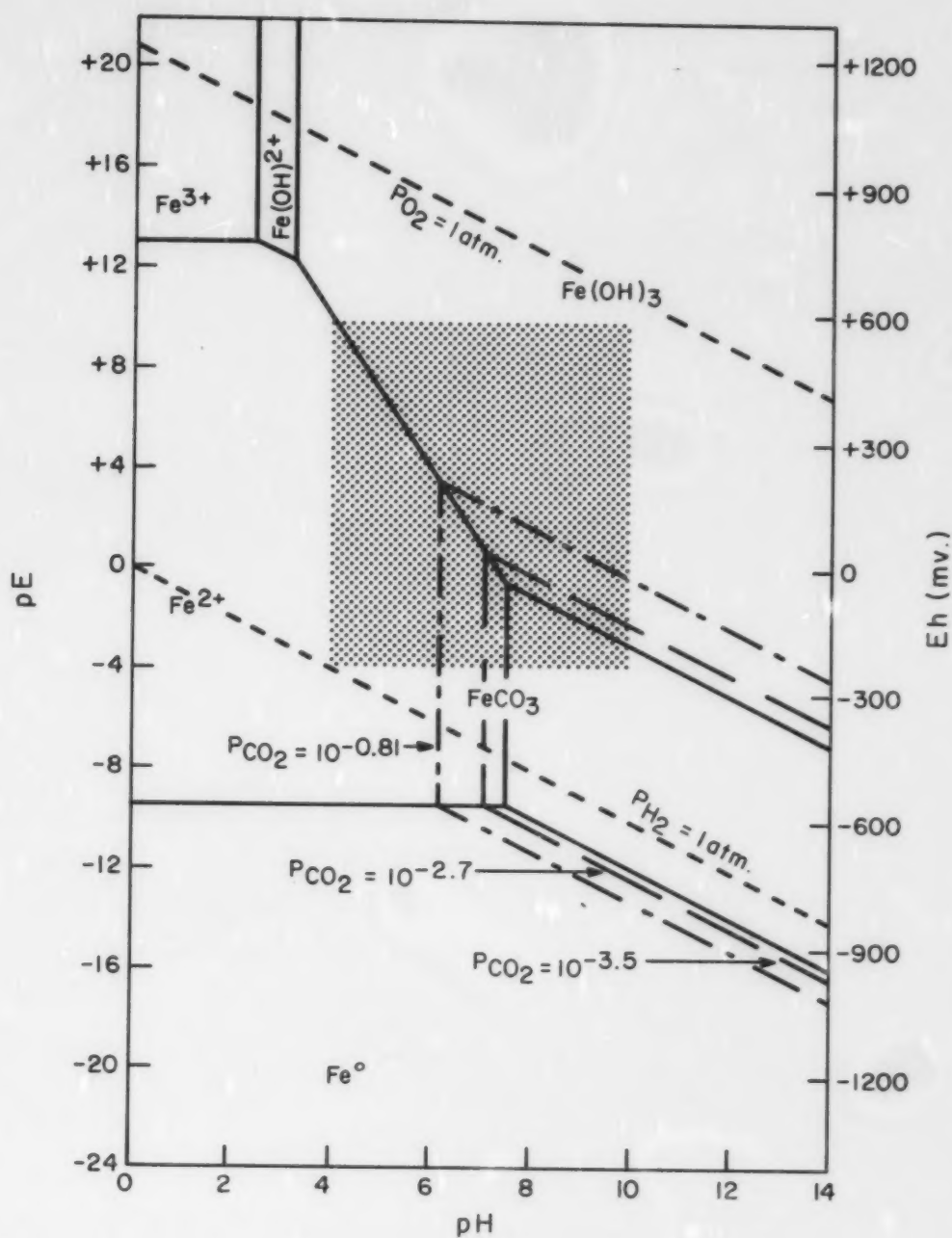


Figure 6.10. Eh (pE) vs. pH stability field diagram for iron ($a_{\text{Fe}} = 10^{-4} \text{M}$; $P_{\text{CO}_2} = 10^{-0.81}$, $10^{-2.7}$, and $10^{-3.5} \text{ atm}$; $P_{\text{tot}} = 1 \text{ atm}$; $T = 25^\circ\text{C}$). (From Jenne, 1968)

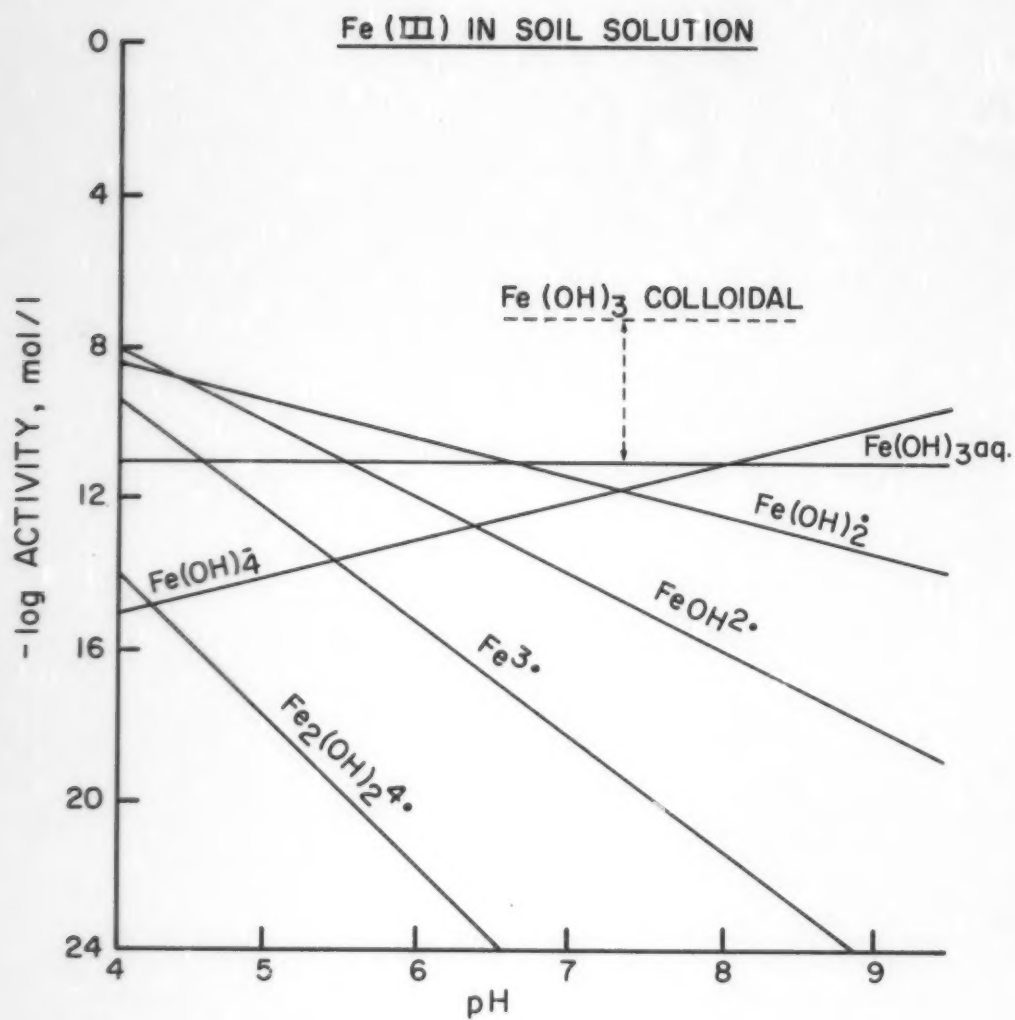


Figure 6.11. The Fe(III) species in solution in equilibrium with hydrous ferric oxides. (From Lindsay, 1972)

SOLUBILITY OF Fe MINERALS

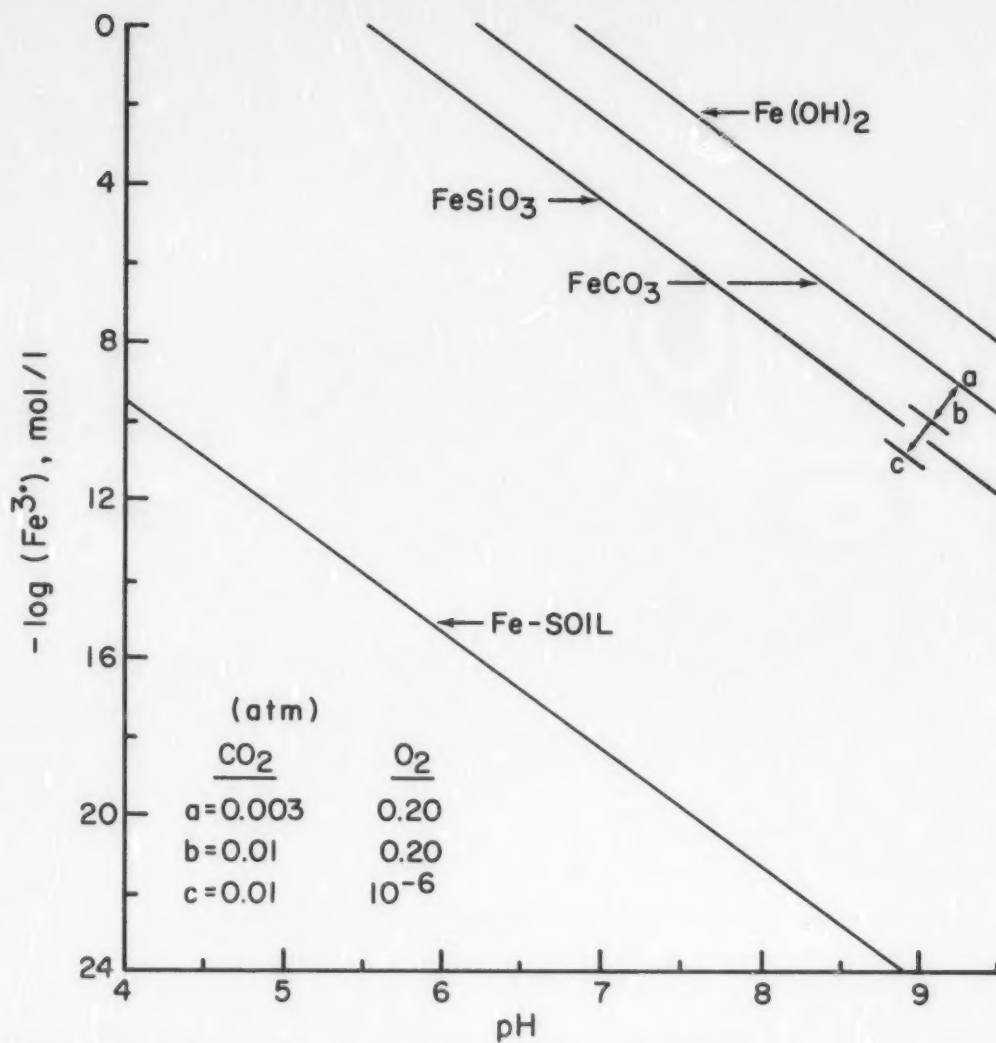


Figure 6.12. The solubility of various Fe(II) minerals compared to that of soil Fe. (From Lindsay, 1972)

according to Lindsay (1972a), "The Fe (II) silicates, carbonates, and hydroxides are too soluble to persist in soil. [i.e., normal aerobic soils] ... They readily dissolve in soils and release Fe^{++} which is oxidized and precipitates as hydrous Fe (III) oxides. [The soil line in Figure 6.12 indicates its solubility.] Small changes in O_2 and CO_2 partial pressure cause only slight shifts in solubility of the Fe (II) compounds compared to the very low solubility of hydrous Fe(III) oxides."

In summary, it should be emphasized that iron is found in great abundance in nature. It appears in most aqueous wastestreams, landfill leachates, and solid wastes in recognizable amounts. In fact, it is a wonder that geologic and recharge subsurface waters are so free of Fe.

The intense reactivity of Fe keeps it remarkably immobile in soils as well as waters. The solubility of Fe in soil depends on the solubility of the hydrous Fe(III) oxides. Under anoxic conditions the solubility of Fe^{++} salts and complexes varies with the partial pressures of CO_2 and O_2 in aqueous solutions. Slight variations can readily cause Fe to precipitate. Further, it should be kept in mind the mobility of Fe is strongly pH-dependent at any Eh level, as oxidation proceeds less slowly with increasing acidity. Iron as hydrous oxides and oxides attracts a host of elements and is involved in attenuation mechanisms for most trace and heavy metals. There appears to be sufficient evidence to support the belief that Fe, Mn, and Al, as hydrous oxides and oxides may be primarily responsible for attenuation or immobilization of most of the potential hazardous pollutants here considered.

LEAD

Lead as a "contaminant" of the human environment and as a potentially hazardous pollutant has long been recognized. Only token abatement measures have been initiated to improve environmental contamination and these only relate to the most obvious sources of pollution. Sources of Pb in the air, waters, and soils have been reviewed by Lagerwerff (1972) as they relate to biological systems and are therefore not discussed here. Suffice it to say

That Pb appears in all areas of our environment (soils, waters, and air) as a "contaminant"; lead in the environment increases in direct proportion to increases in population. The obvious most serious pollution originates from energy consumption, primarily fossil fuel utilization. Lead concentration in soils is given in Table 6.6 as varying from 2 to 200 ppm (Allaway, 1968).

TABLE 6.6. HEAVY METAL CONTENT IN SOILS AND PLANTS*

Metal	Soils		Plants	
	Typical	Range	Common Range	Toxic limits (Using recent work)
	ppm	ppm	ppm	ppm
Cadmium	0.06	0.01-7	0.2-0.8	-
Cobalt	8	1-40	0.05-0.5	-
Copper	20	2-100	4-15	30
Lead	10	2-200	0.1-10	-
Manganese	850	100-4000	15-100	-
Nickel	40	10-1000	1	25
Zinc	50	10-300	8-15	500

* From Allaway (1968).

Lead, like many heavy metals, is present in soils as a cation which precipitates easily as sulfide, hydroxide, and carbonate. Lead also is subject to surface adsorption, particularly on aluminum silicates. Comparing Pb with some other metal cations, sorption occurs more strongly in the general order of $\text{Cu}^{++} > \text{Pb}^{++} > \text{Ni}^{++} > \text{Co}^{++} > \text{Zn}^{++}$. There is a great affinity between Pb and organic matter for retention or immobilization (attenuation) against migration.

In an extensive study of soils and their properties in relation to Pb availability to plants, John (1972) concluded that Pb availability is related to soil pH, extractable Al, and total Ni (Table 6.7). He found no observable relationship with soil organic matter. Plant availability

TABLE 6.7. SELECTED SOIL PROPERTIES AND RESULTS OF SOIL AND PLANT LEAD ANALYSES*

Location and soil order ^a	Soil type	pH in water (PHW)	Organic matter (%)	Clay fraction (CLAY)	Lead extracted from soil with 1 N HNO ₃		Lead content of plants when 500 ppm Pb added to soil
					Check soil	Incubated with 500 ppm Pb	
					-----ppm-----		
F VII	Benson si.l.	5.3	6	9	21	493	76
F VII	Delta si.c.l.	7.2	5	17	102	493	23
F VII	Ladner si.c.l.	4.9	12	11	1	507	58
F VIII	Lulu muck	5.1	35	19	13	429	25
F VII	Vinod muck	5.0	36	20	13	482	116
F VIII	Lumbum muck	4.4	61	20	13	446	29
F VII	Annis muck	4.5	36	21	10	550	96
F VI	Fairfield si.c.l.	5.4	5	35	10	457	51
F VI	Grevell s.	7.2	1	1	6	518	38
F VI	Monroe si.l.	5.7	3	13	7	486	47
F VII	Buckerfield si.l.	5.7	7	32	10	536	59
F V	Marble Hill s.l.	5.7	6	35	8	443	44
F VI	Sumas s.	5.6	1	3	4	500	107
F VII	Vedder si.l.	6.2	4	23	10	500	34
F V	Abbotsford s.l.	5.2	6	6	8	432	21
F V	Whatoom si.l.	5.7	7	25	36	529	103
F VII	Cloverdale si.l.	5.6	10	21	6	482	50
F VII	Langley l.	5.5	16	20	2	479	51
F V	Milner l.	5.7	8	15	10	464	73
F V	Nicholson l.	5.7	5	15	8	442	36
F V	Sunshine l.s	5.5	10	6	8	421	49
F VII	Hjorth l.	5.0	17	38	9	507	57
F VI	Monroe si.l.	5.7	3	30	8	482	45
F VII	Page si.l.	5.8	4	36	7	482	55
F V	Ryder v.f.s.l.	6.5	8	8	7	493	23
O II	Glenmore si.c.	7.3	4	66	14	489	36
P III	Alcan si.l.	6.1	8	35	7	550	36
C III	Vanderhoof si.c.l.	6.5	1	45	7	482	45
N V	Selwyn s.l.	5.0	2	4	6	471	76
	Mean	5.7	11	20	13	484	54
	Standard deviation	0.7	14	15	18	34	26

* Adapted from Matt K. John (1972).

[@] Location: F, Fraser Valley, B.C.; O, Okanagan Valley, B.C.; P, Peace River Area, B.C.; C, Central Interior B.C.; N, New Zealand.

Soil order: I, Chernozemic; II, Solonchic; III, Luvisolic; IV, Podzolic; V, Brunisolic; VI, Regosolic; VII, Gleysolic; VIII, Organic.

information is mentioned as a possibility for providing clues to Pb mobility and attenuation in soils.

Because many wastes are applied to the soil under conditions conducive to waterlogging and the creation of anoxic conditions, the studies by Kee and Bloomfield (1962) should be pointed out. They found that naturally occurring Fe, Co, Ni, Zn, Pb, V, and Mo in soils became more mobile when soils were flooded and incubated anaerobically with organic residues (plant debris). Chromium but not chromite was also mobilized.

Both hydroxy and chloride complexes appear to influence the mobility of Hg (II), Cd (II), and Pb (II) in soils, according to Hahne and Kroontje (1973). Hydrolysis of Pb (II) becomes important at pH values above 5. Lead is in the form of hydroxy complexes at a pH value of 8.5 and Cl concentration of 350-60,000 ppm in contrast to Hg (II) and Ce (II) which are complexed by Cl.

In aqueous wastes containing organic matter, organo-metal-complexes may form. Certainly they form in soils containing organic matter and may exist as soluble chelates or colloids; lead is no exception, Brown (1969), Lindsay and Norvell (1969), Schnitzer (1969), Wallace (1963), and Stevenson and Ardashkani (1972). Some evidence is presented indicating that soil organic matter chelates of Pb are of low solubility.

Soluble Pb, reaching the soil from aqueous wastestreams, is expected to form compounds of low solubility readily with $\text{SO}_4^{=}$, $\text{CO}_3^{=}$, or PO_4^{3-} anions.

Lagerwerff (1972) suggests the following as means of Pb abatement: "... liming reduces the uptake by plants from soil. This may be due to several reasons. The ensuing increase in soil pH may result in precipitation of Pb as the hydroxide, carbonate, and phosphate. The Ca ions will compete with the trace amounts of Pb present for exchange sites on the soil and root surfaces. The increased pH and Ca^{++} activity may diminish the physiological capability of plant roots to absorb Pb. Finally, liming may promote the capacity of organic matter to form complexes with Pb."

MERCURY

One of the most complete reviews on mercury in the environment is that of D'Itri (1972). Because this review was supported by the Michigan House of Representatives Great Lakes Contamination (Mercury) Committee, the Data and examples provided in the manuscript are highly localized for the Great Lakes area. This does not imply, however, that the basic principles of mercury behavior in the environment, as provided in this document, cannot contribute to understanding other environments. Indeed, some of the data may have world-wide application. Information from this book, which is well documented and international in scope, is not repeated here. This book is an excellent supplement to this manuscript for those who wish a more thorough insight into the subject of mercury.

In addition to D'Itri's (1972) review, Jenne (1970) and the manuscript of Jonasson and Boyle (1971) are suggested for reading.

The chemical behavior of Hg in the environment also has been reviewed by Bondietti et al. (1973). Some of their comments are:

"The oxidation states (sic) of Hg, 0, +1, and +2, occur in nature depending on the oxidizing conditions of the local environment. In aerated water and in nearly neutral solution Hg⁰ is stable and the soluble inorganic mercury is in the +2 oxidation state. Elemental mercury forms only when the activity of oxygen is less than 10^{-20} atm (or reducing conditions). The solubility of Hg⁰ was recently estimated at 2.8×10^{-7} M (~ 50 ppb), Spencer and Voigt (1968).

"Mercuric ion, Hg²⁺, hydrolyzes to give the species: Hg(OH)⁺, Hg(OH)₂, Hg₂(OH)³⁺ and Hg₃(OH)₃³⁺ and probably Hg(OH)₃⁻ in very basic solutions. ... Our reexamination of the data of Ahlberg (1962) in relatively concentrated mercury solutions has led us to propose the trimeric species to replace the two species Hg₂(OH)₂²⁺ used by Ahlberg (1962). Also Johansson's (1971) recent X-ray diffraction data on

solutions indicate that the polymeric species contains two Hg neighbors as would be expected for the trimer.

"The neutral dissolved species, $\text{Hg}(\text{OH})_2$, has exceptional stability and exists at pH values above 4 when other complexing reactions do not compete. The most stable oxide phase at 25°C is orthorhombic HgO. The red and yellow oxides are but different particle sizes of this form and the minimum solubility of the red HgO at 25° is 2.4×10^{-4} M. Obviously, natural waters will not be saturated with respect to this form if, indeed, they are saturated with respect to any solid phase. The sulfide is very insoluble and forms when appreciable levels of $\text{S}^{=}$ are present. As with other trace metals the interactions with the biota and the exchange with sediments or dispersed minerals or clays are not well understood.

"The methyl mercury ion, $\text{CH}_3\text{Hg}(\text{H}_2\text{O})^+$, hydrolyzes to form CH_3HgOH and the species $(\text{CH}_3\text{Hg})_2\text{OH}^+$, at concentrations in excess of 10^{-3} M (200 ppm as Hg). Above pH 6 methyl mercury exists as the natural species, CH_3HgOH , in the absence of other complexing agents, Schwarzenbac and Schellenberg (1965). The complexes of CH_3Hg^+ with $\text{S}^{=}$ and S-containing ligands are uniquely stable. Other alkyl mercury ions have complexing properties similar to the methyl derivative for OH^- , Br^- , and Cl^- . The thermodynamic stability of the CH_3Hg^+ ion toward decomposition to methane is not known, but it is presumed to be unstable. The kinetics of this decomposition has not been studied, although CH_3Hg^+ appears to be stable for long periods at ordinary temperatures."

Mercury is present in the outer earth's crust, in most common ores, and gangue materials ranging from about 0.01 to several hundred ppm. Mercury also is present in soils at lesser levels, probably between 20-150 ppb with a mean value of about 70 ppb (Table 6.8). Airborne Hg deposits itself in the surface of soils along with the natural sources present. The soil organic matter attenuates Hg to the extent that Hg concentrates in or on soil surfaces. In natural water sources, free of Cl, Hg^0 predominates as

TABLE 6.8. MERCURY CONTENT OF SOILS AND GLACIAL MATERIALS*

Description	Range	Mean
	ppb	ppb
Normal soils	20 - 150	70
Normal tills, glacial clay, sand, etc.	20 - 100	50
Soils, tills, etc., near mercury deposits, sulfide deposits, etc.	up to 250 ppm	
Soil horizons (normal) ^⑥ : A (humic)	60 - 200	161
B	30 - 140	89
C	25 - 150	96
Soil horizons (near mercury deposits) :		
A (humic)	200 - 1,860	480
B	140 - 605	475
C	150 - 554	263

* From Jonasson and Boyle (1971).

^⑥ Examples from Clyde Forks area, Ontario.

a species. Concentration values of Hg in these waters, with only a few exceptions, fall below 5.0 ppb, the threshold value for acceptability as drinking water, Lagerwerff (1972).

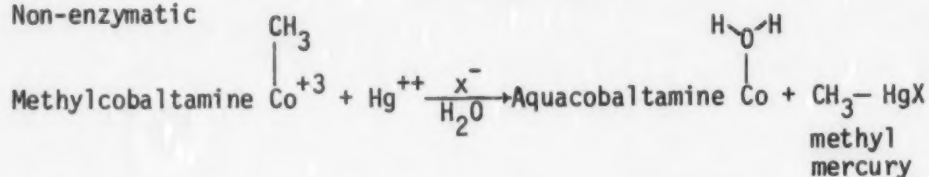
Mechanisms of attenuation (immobility) in soils include (a) valence-type ionic adsorption by organic and inorganic materials (b) formation of covalent bonds with organic compounds, (c) formation of low solubility Hg salts of phosphate, carbonate, and sulfide.

Transformations in Soils

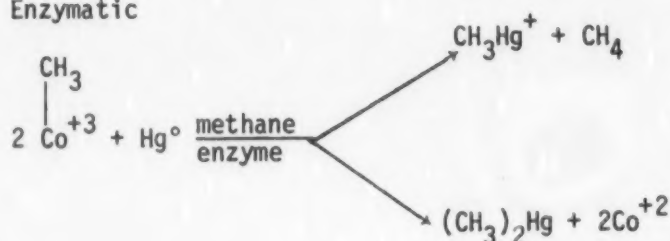
A fairly large volume of literature is available specifically concerned with mercury in soils. There is also a great deal more information that may be related to soils, but, unfortunately, there is no agreement on the fate and movement of mercury in the soil environment. There is no doubt

that inorganic mercury in sediments, lake bottoms, etc., is methylated to mono- or di-methyl mercury, Wood et al. (1968), Jenson and Jernelov (1969). Wood et al. (1968) have shown that Methanobacterium omelianskii, which forms an integral part of a sludge ecosystem, methylates mercury through one of two processes:

(1) Non-enzymatic



(2) Enzymatic



In the non-enzymatic process, the methyl group is transferred as an anion from Co^{+++} to Hg^{++} . Methylcobaltamine is a common co-enzyme in both anaerobic and aerobic bacteria. Thus, significant quantities of methyl- B_{12} derivatives are present in sludge promoting this transfer.

For the enzymatic process, there is first the chemical reduction of Hg^{++} to Hg^0 . Then, depending on the concentration of Hg^0 and pH, dimethyl and/or monomethyl mercury are formed as products.

This allows loss of Hg from the systems in several ways. As will be seen, all of the products (including Hg^0) are volatile, water-soluble, or both.

Landner (1971) has presented evidence that Neurospora crassa can methylate mercury aerobically without methylcobaltamine. Furthermore, Komura et al. (1970) state that types of coli bacteria can reduce Hg^{++} to

the volatile metal. Escherichia coli is an example of a bacterium derived from fecal sources and apt to be found in pollutant systems.

Hem (1970) presents an Eh-pH diagram demonstrating that Hg^0 is slightly soluble. This characteristic is used in the flameless atomic absorption technique for the analysis of mercury. The technique depends upon the high vapor pressure of metallic mercury. Thus, if Hg^0 appears in a solution flushed with a gas, the volatile metal is removed. This occurred when landfill leachate in the Arizona lab was flushed continuously with CO_2 . Thus, any organic transformation or chemical reduction of Hg^{++} inorganic ions can lead to a Hg loss from the leachate, Niebla et al. (1976, in press).

Lagerwerff (1972) states that the ionic monomethyl compound is soluble in H_2O and complexes with anions. The molecular dimethyl compound is relatively insoluble in H_2O and escapes as a vapor. The formation of monomethyl mercury apparently requires acidic conditions and high concentrations of Hg^{++} . This indicates Hg loss due to volatilization of Hg^0 or dimethyl mercury. It has also been reported that Pseudomonas vaporizes Hg and removes it from wastes, Suzuki et al. (1969). Kimura and Miller (1964) state that monomethyl mercury compounds are by themselves volatile, presenting another mechanism of mercury loss. This is in contrast to what Lagerwerff reported. It seems likely that monomethyl compounds are stable in water because of the high concentrations of methyl mercury found in fish taken from water polluted with mercury.

Some very interesting results have been reported by Frear and Dills (1967) regarding the use of inorganic mercury salts as insecticides. They discovered that mercury vapor was the lethal agent in the insecticide. They mixed mercuric salts with soils to determine the effects of organic matter, temperature, soil pH, and moisture content. If a soil was ignited to remove organic matter, no mercury vapor was produced -- no insects were killed. They also found that low moisture content inhibits reduction. Moisture content of 17% and greater gave rapid reduction. Mercuric reduction also increased with increasing soil pH. Soil pH of 5.25 provided little or no reduction. Furthermore, the maximum rate of

transformation was attained at 25°C with reduction being limited at temperatures less than 10°C. Insect eggs were killed when suspended over a pool of mercury vapor, indicating that elemental mercury was coming off the soil. Although the experiments were not analytical in nature, they serve to point out that mercury escapes very easily from soils.

Despite the fact that most landfills are located in inorganic subsoils and inorganic geologic materials, organic matter still is a key factor in Hg mobility through soils, Niebla et al. (1976, in press). Landfill leachates are abundantly supplied with organic constituents, acids, and heterogeneous organic debris at various stages of degradation and subparticle division. These may exist as soluble or colloidal forms and therefore differ in rates of migration, Hahne and Kroontje (1973). Though Hg in aerobic (oxic) soils may persist in any form, under anaerobic, anoxic, waterlogged and water-saturated conditions, at least some Hg will be converted by anaerobic bacteria into soluble monomethyl or gaseous dimethyl Hg complexes. It should be pointed out that in the case of Hg it is well known that alkyl mercury compounds such as methyl mercury are far more toxic than ordinary Hg salts. On the other hand, if mercury complexes with larger functional groups, such as aryl or alkoxyalkyl compounds, toxicity is less (Lagerwerff 1972).

Reactions such as : $\text{Hg}_2^{2+} = \text{Hg}^{2+} + \text{Hg}^0$ occur readily in soils.

Soil-mercury reactions, as pointed out by the voluminous literature on the subject, seem to be dominated by mercury-organic interactions, Baes and Mesmer (1973).

Free Hg or Hg^0 produced under anaerobic conditions becomes available, however, for conversion to HgS . Under certain alkaline conditions, HgS may be converted into Hg_2S , which is soluble.

Anionic HgCl_3^- and HgCl_4^{2-} and molecular Hg_2Cl_2 and HgCl_2 may adsorb to particle coatings of hydrous oxides of Fe and Mn, Jenne (1968).

Movement and Retention in Soils

Much work on mercury has been undertaken by Anderson et al. (1961). They stated that under acidic aerobic conditions with sufficient chloride present, the predominant Hg species in soil solution is HgCl_2^0 . While this species is only slightly adsorbed, elemental mercury is strongly adsorbed by Fe-oxides and also scavenged by organic matter. The latter process occurs most readily at low pH. As the pH increases Hg is more readily adsorbed on soil minerals, Anderson (1967).

Aomine et al. (1967) report that Hg is adsorbed most on allophanic soils. Allophane is an amorphous mineral which forms under conditions of medium to high hydromium ion concentrations in highly moist systems by rapid weathering of non-crystalline volcanic ash or rapid weathering of feldspars. Allophane can be described as an amorphous alumino-silicate with which abundant organic matter is complexed in the upper layers, Buol, Hole, and McCracken (1973). Possibly adsorption of Hg by allophane is a further manifestation of the role of organic matter.

Strohal and Makhonia (1971) found that competing cations had no effect on the release of organically complexed mercury. They extracted soil with H_2O and with H_2O containing varying amounts of leaf extracts. As the amount of organic matter increased, the amount of mercury released from the soil increased. This is direct evidence that mercury is more mobile in soil if it is organically complexed.

Several studies have been made of the fungicide, phenylmercuric acetate (PMA). Kimura and Miller (1964) state that PMA degraded to Hg^0 in the soil and was lost as Hg vapor. They also reported that the tendency of Hg to escape increased at low soil moisture. This contradicts Frear and Dills' (1967) finding that inorganic mercury was reduced most easily at high soil moisture. Another anomalous finding is that air drying soil samples results in no Hg loss, Hamm and Stewart (1973). It should be noted that this experiment dealt with "naturally abundant" mercury. Aomine et al. (1967) and

Inoue et al.(1969) have worked extensively with PMA. They found that it did not migrate down into the soil upon which it was applied. In each case (except with a sandy, very porous soil), no Hg or PMA was found in sub-surface horizons. There was no way to tell from the work how much mercury was lost by volatilization.

It is rather difficult to summarize findings such as these. The only safe assumption is that mercury applied to the environment will not remain in the same state as applied.

There is ample evidence that mercury applied directly to soils is volatilized, probably as Hg^0 . Mercury found in a strictly reducing environment, such as in a sludge or in a landfill, is alkylated. There is apparently no available data on the amount of methyl mercury in soils. It appears that from the landfill standpoint, this is the most important species. Any Hg^0 or dimethyl mercury formed will be expelled as a gas. Inorganic mercury can be precipitated as a sulfide and probably does not migrate greatly. However, in any system containing ample organic matter, the mercury can be complexed and transformed in a variety of ways. Of the metals being considered in the landfill project, mercury is clearly the most complicated.

For the most part, Hg attenuation or movement in soils must relate to organic carbon or sulfur chemistry either separately or together as humic substances containing S. Some biologically oriented cycles have been prepared by Jonasson and Boyle (1971) and are reproduced here as Figures 6.13-6.15.

SELENIUM

A number of good references exist on the subject of selenium mineralogy, and one of particular interest is by N.O. Sindeeva (1964).

Selenium is widely distributed over the earth's surface crust as selenites and selenates of sodium and calcium. Some Se also occurs as

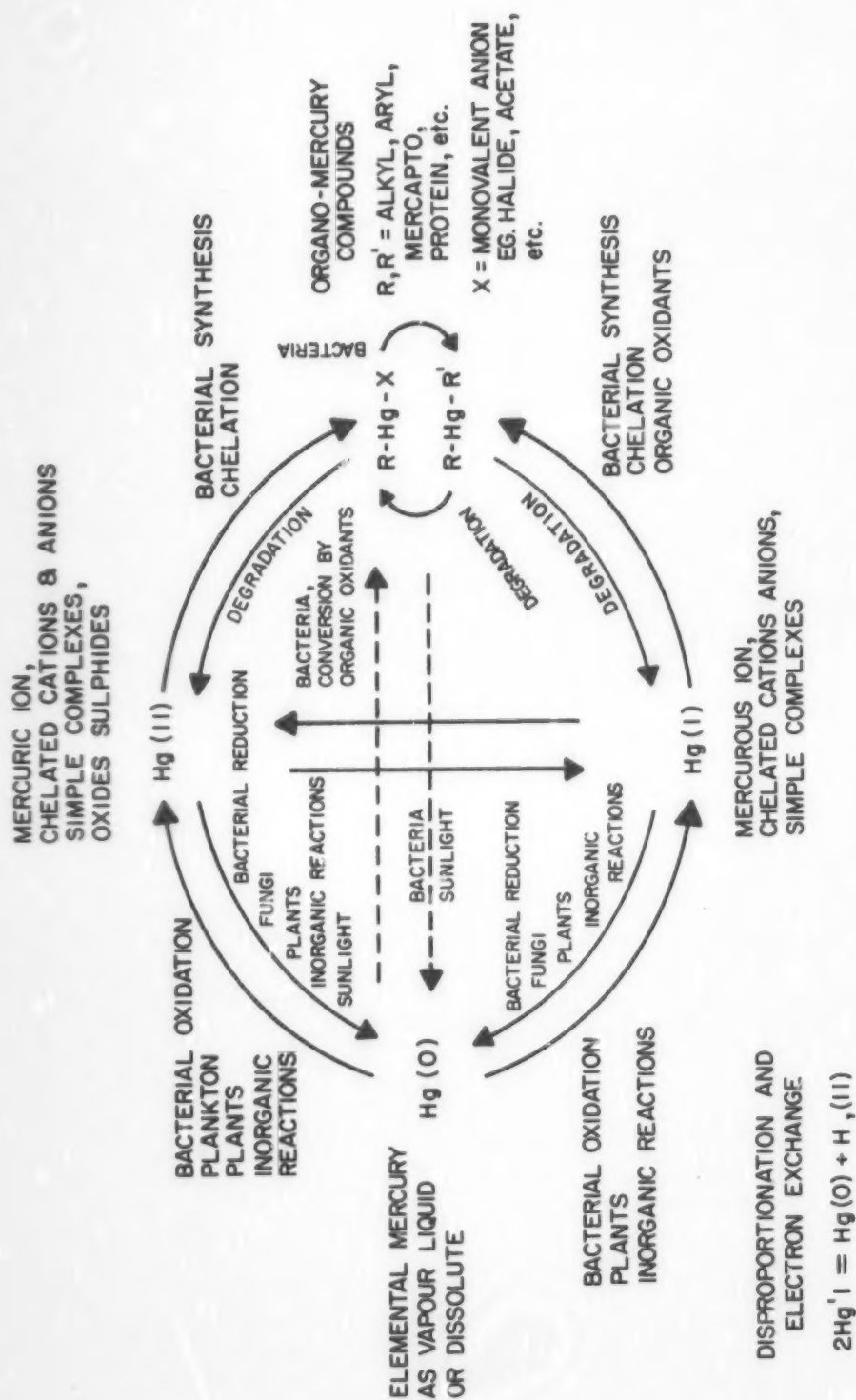


Figure 6.13. The cycle of mercury interconversions in nature. (From Jonasson and Boyle, 1971)

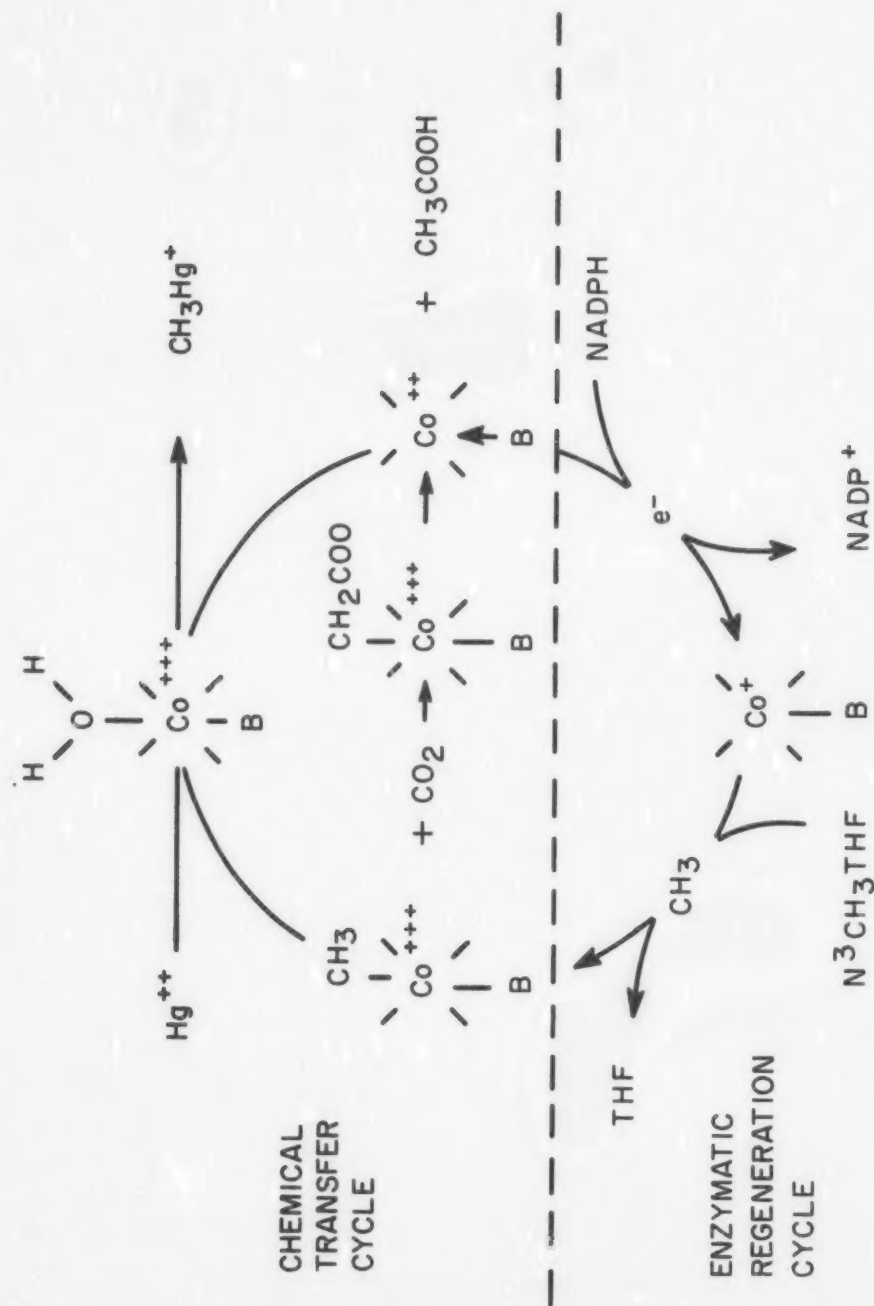


Figure 6.14. An anaerobic biological synthesis mechanism for methyl mercury. (From Wood et al., 1968)

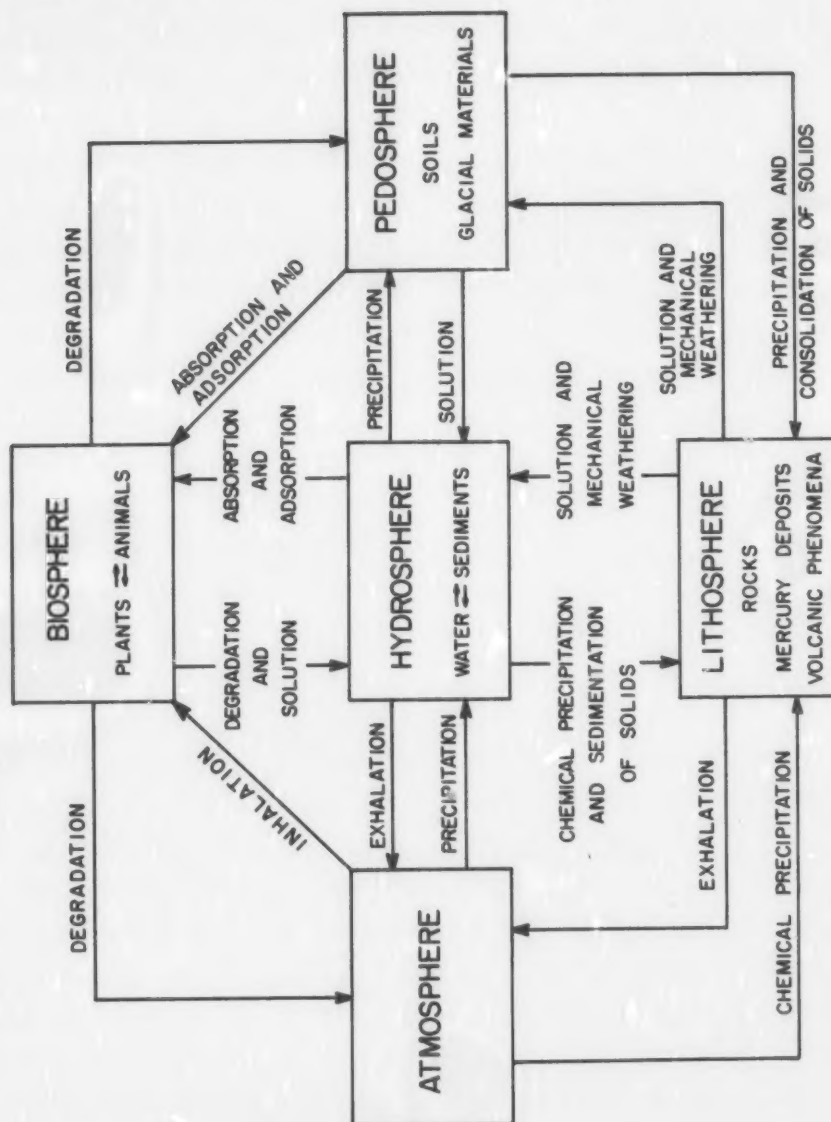


Figure 6.15. Generalized geochemistry cycle in mercury. (From Jonasson and Boyle, 1971.)

sparsely soluble basic salts of Fe. The presence of organic Se-containing compounds has been established in soils. According to Sindeeva (1964) the process of oxidation and reduction may be repeated several times under the action of soil microorganisms and atmospheric agents.

Selenium is used in the glass industry, electrical engineering, television, steel, rubber, photography and numerous other branches of industry.

Selenium is closely related to sulfur both chemically and biologically. The latter because it can substitute for S in biological assimilation and in organic molecule substitution. Also like sulfur, it has six electrons in the outer shell, making it metalloid. Upon the addition of two more electrons, selenium is transformed into negative bivalent ions, in which form it combines with metals and forms selenides. In combination with O_2 , the valencies of 4^+ and 6^+ are expressed. Like sulfur, selenium forms dioxides and trioxides and the corresponding acids -- selenious and selenic. The salts of these acids form similarly to sulfurous and sulfuric acid. Metals of Cu, Pb, Ni, and others in soils form from the action of selenious acids. These are stable in soil. Salts of selenic acid rarely appear in nature. If they form, they readily reduce to selenites and/or to free selenium, Sherilla and Isard (1928).

The equilibrium states of Se are diagrammed by Delahay, Pourbiax, and Van Ryselberghe (1952) and are reproduced as Figure 6.16. The diagram shows pH values 0 to 14 plotted in relation to $Eh(V) - 0.55$ to $+ 1.25$ at $+ 25^\circ$, 1 atm. pressure, and concentration of Se at 10^{-6} moles. The two lines having dashes are included to point out assumed boundaries of normal earth surface conditions. Selenium is highly pH sensitive. Lakin (1961) and Lakin and Trites (1958), who have studied Se in soils, conclude that the ferric hydroxide in acidic or neutral soils provides an important mechanism of precipitation which not only attenuates Se but substantially reduces uptake by plants. In some soils, reduction of Se to elemental Se also provides an effective mechanism of attenuation. Selenate is the available form of Se in alkaline soils, Brown and Carter (1969). Less selenium is available to plants at lower pH, indicating decreased mobility. Preliminary

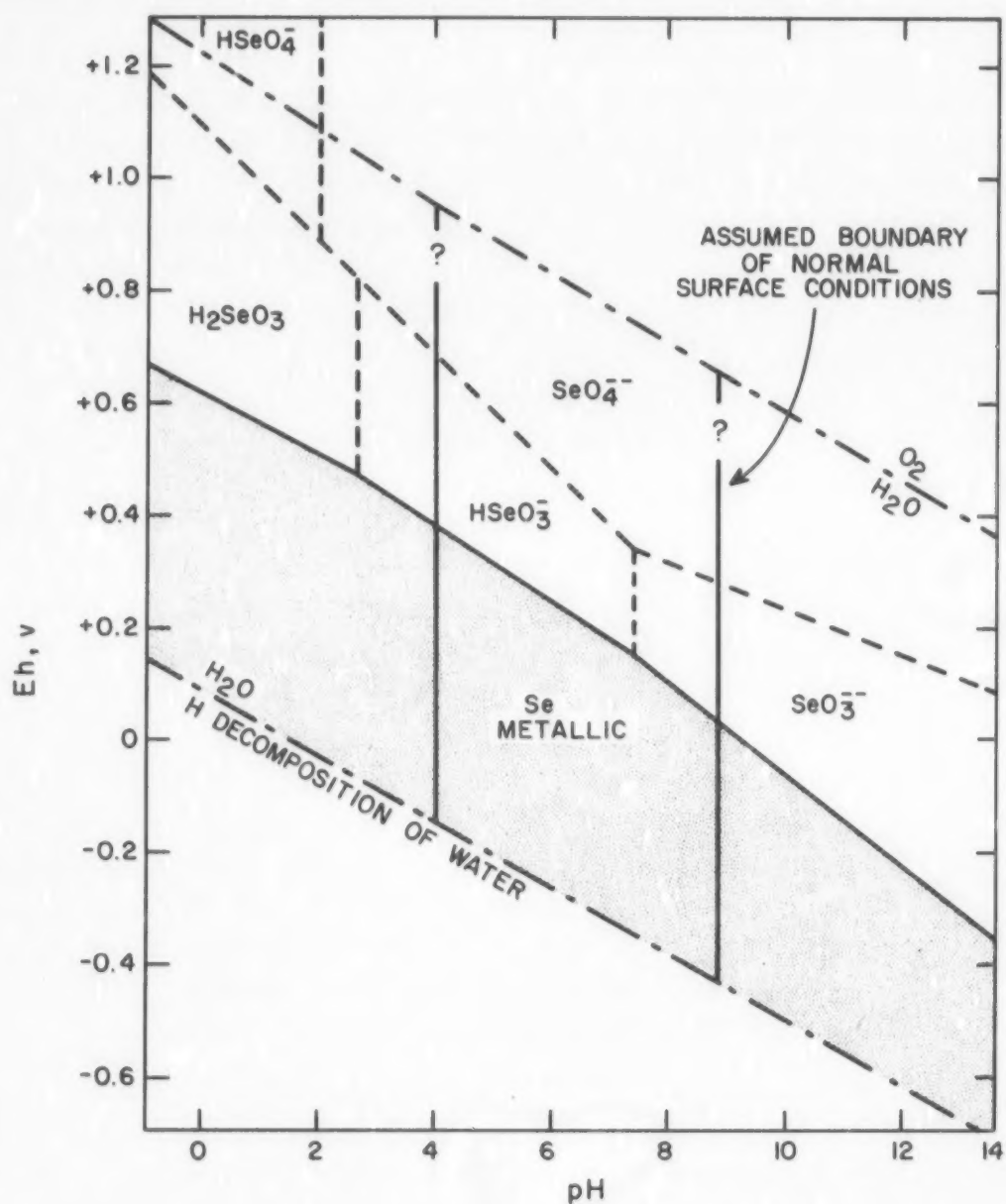


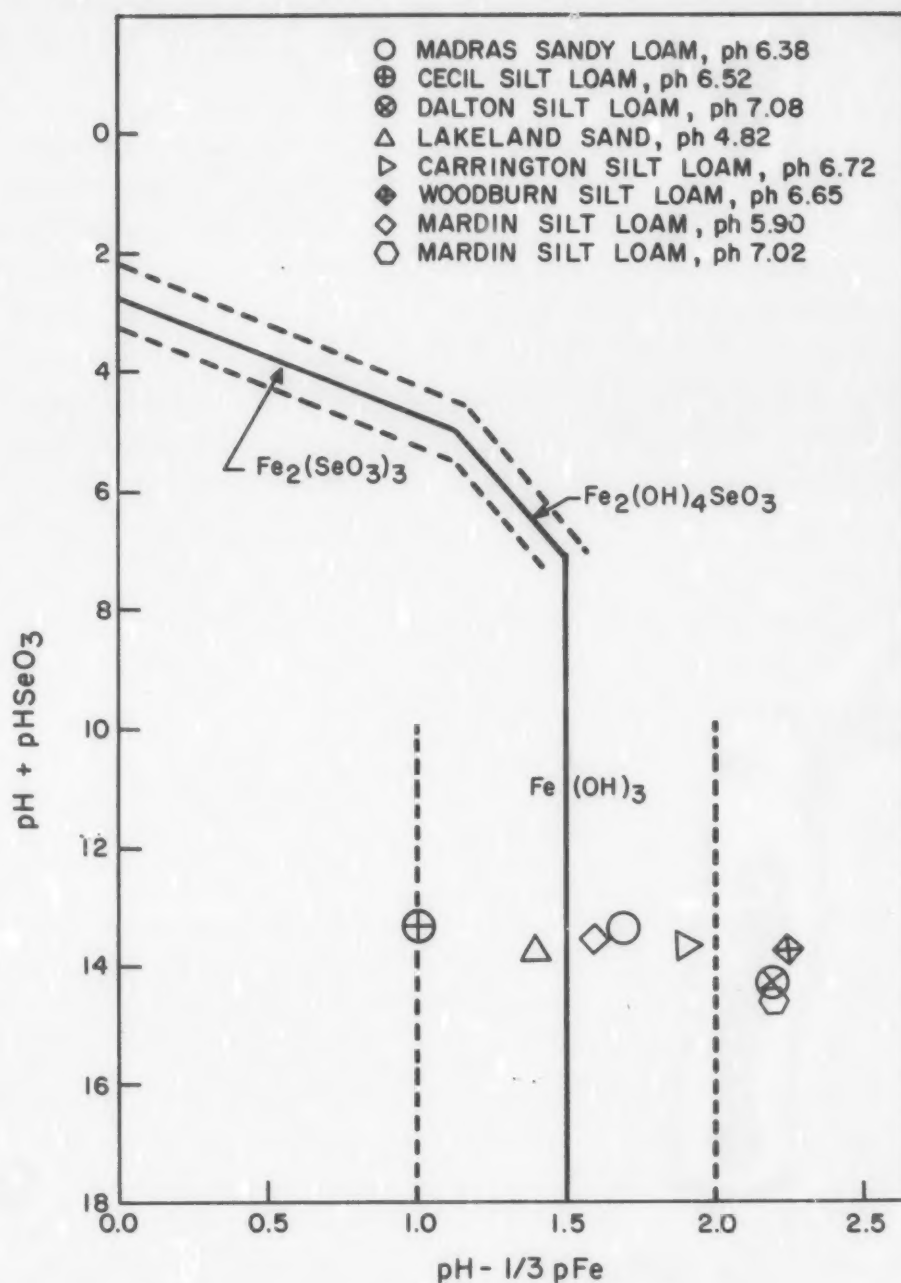
Figure 6.16. Stable fields of selenium. (Data from Delahaye, Pourbaix, Van Russelberghe, diagrammatically arranged by Coleman.)

data from the University of Arizona study support the finding that, other factors being equal, selenium is less mobile in acidic than in neutral to alkaline soils.

Geering et al. (1968) furnish evidence that Se concentration in the solution of seven soils is governed primarily by ferric oxide-selenite-adsorption complex (Se oxidation state +4). They show Se can also exist in the oxidation states of +6, 0, and -2. They approached the problem of identifying the selenites that may exist in a soil by obtaining values for the activities of selenite, ferric and hydrogen ions in soil solution extracts and referring these values to a solubility diagram of the ferric selenites. (Figure 6.17). The selenious acid potential ($\text{pH} + \text{pH SeO}_3$) is plotted against the ferric hydroxide potential ($\text{pH} - 1/3 \text{pFe}$). They have this to say about the data plotted in Figure 6.17:

"Had the points fallen along one of the ferric selenite lines, this would indicate that a crystalline ferric selenite could exist in the soil. Had the points fallen in the region below the ferric selenite lines and to the left of the ferric hydroxide lines, this would indicate that a crystalline ferric selenite could exist in the soil. Had the points fallen in the region below the ferric selenite lines and to the left of the ferric selenite lines, this would indicate that the selenite Se in these soils may be present in less soluble forms than the ferric selenites considered here. Less soluble forms of selenite could arise through the formation of (i) less soluble crystalline ferric selenites, and (ii) anomalous solid solutions of the ferric selenites in ferric hydroxide.

"For the most part, the experimental points fell along the ferric hydroxide line and below the ferric selenite lines. This indicates that crystalline ferric selenites are probably not governing the observed Se solubility in these soils. If part of the selenium measured in the soil solution extracts were in some form other than selenite, the experimental points [...] would again be located along the ferric hydroxide line but fall still further below



(pH VALUES WERE MEASURED ON AN EQUILIBRIUM 1:10
SOIL - 0.01 $\text{M Ca}(\text{NO}_3)_2$ EXTRACT)

Figure 6.17. Solubility diagram for the ferric selenites, and the solubility data obtained from 1:10 soil-0.01 $\text{M Ca}(\text{NO}_3)_2$ extracts of seven soils shown in Table. (From Geering et al., 1968)

the ferric selenite lines. Thus, the evidence would be even stronger that the solubility of Se in these soils is not controlled by the crystalline ferric selenites indicated [...].

"The points that fell to the right of the ferric hydroxide line were due to the fact that the Fe^{3+} ion activity values estimated in the soil extracts were higher than those predicted by the activity product of ferric hydroxide. This may have resulted from the complexing of Fe^{3+} ions by soluble ligands in the soil, or simply from the possibility that the soils extracts were supersaturated with respect to ferric iron. In such instances, the method used to calculate the Fe^{3+} activity from total iron measured in solution was not appropriate.

"Additional evidence [in Table 6.10] appears to support the contention that selenite may form adsorption complexes with ferric oxides in soils rather than a crystalline ferric selenite. Apparently, anions which tend to dissolve ferric precipitates through complexing of ferric ion, such as EDTA and citrate, are less effective in solubilizing radioactive selenite in soils than are anions such as 'cold selenite', arsenate, arsenite and phosphate, which tend to form adsorption complexes and/or precipitates with ferric ion. The mechanism by which these anions are effective may involve selenite replacement, which would be greater if selenite ions were surface-adsorbed than if they were in crystal lattice of a pure compound." (See Tables 6.9 and 6.10).

For reactions of Se in soils at other valencies (i.e., SeO_4^{2-} , Se^0 or Se^{2-}) than $4+$, Geering et al. (1968) compared Eh as a function of pH for some redox couples that may influence Se oxidative states (and mobility) in soils. They plotted the Eh dividing line between oxidized and reduced soils, according to Pearsall (1938), as a dashed line. Their comments regarding Figure 6.18 are as follows:

"Above this [dashed] line are drawn the redox couples for $\text{O}_2/\text{H}_2\text{O}$, $\text{MnO}_2/\text{Mn}^{2+}$, and $\text{SeO}_4^{2-}/\text{SeO}_4^{2-}$. Intersecting this line are

TABLE 6.9. MEASURED VALUES OF Eh, pH and TOTAL ^{75}Se , Fe CONCENTRATIONS OF A 1:10 SOIL-0.01 M $\text{Ca}(\text{NO}_3)_2$ EXTRACT FOR ESTIMATING pH+ pHSeO_3 and pH-1/3 pFe*

Soil	pH	Eh mv	(^{75}Se) total $\text{M} \times 10^8$	(Fe) total $\text{M} \times 10^8$
Madras sandy loam	6.38	600	9.8	9.8
Cecil sandy clay	6.52	590	12.4	1.0
Dalton silt loam	7.08	575	3.2	15.0
Lakeland sand	4.82	665	5.7	15.0
Carrington silt loam	6.72	570	8.9	7.6
Woodburn silt loam	6.65	590	8.6	79.0
Mardin silt loam	5.90	605	2.1	8.5
Mardin silt loam	7.02	565	4.2	106

* From Geering et al. (1968).

TABLE 6.10. PERCENT ^{75}Se EXTRACTED FROM 0.8-g SUBSAMPLES OF WOODBURN s1 BY 8 ml OF 0.1 N ANION SOLUTIONS IN 1 M KNO_3 DURING 24 HOURS AT 25C*

Anion	Source	% ^{75}Se Extracted
Selenite	H_2SeO_3	33.1
Fluoride	NH_4HF_2	26.6
Arsenate	As_2O_3	20.0
Arsenite	As_2O_3	19.2
Phosphate	KH_2PO_4	18.2
Citrate	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$	13.5
Molybdate	MoO_3	8.1
EDTA	EDTA	7.3
Sulfate	K_2SO_4	6.3
Nitrate	KNO_3	6.3
Chloride	KCl	5.5

* From Geering et al. (1968).

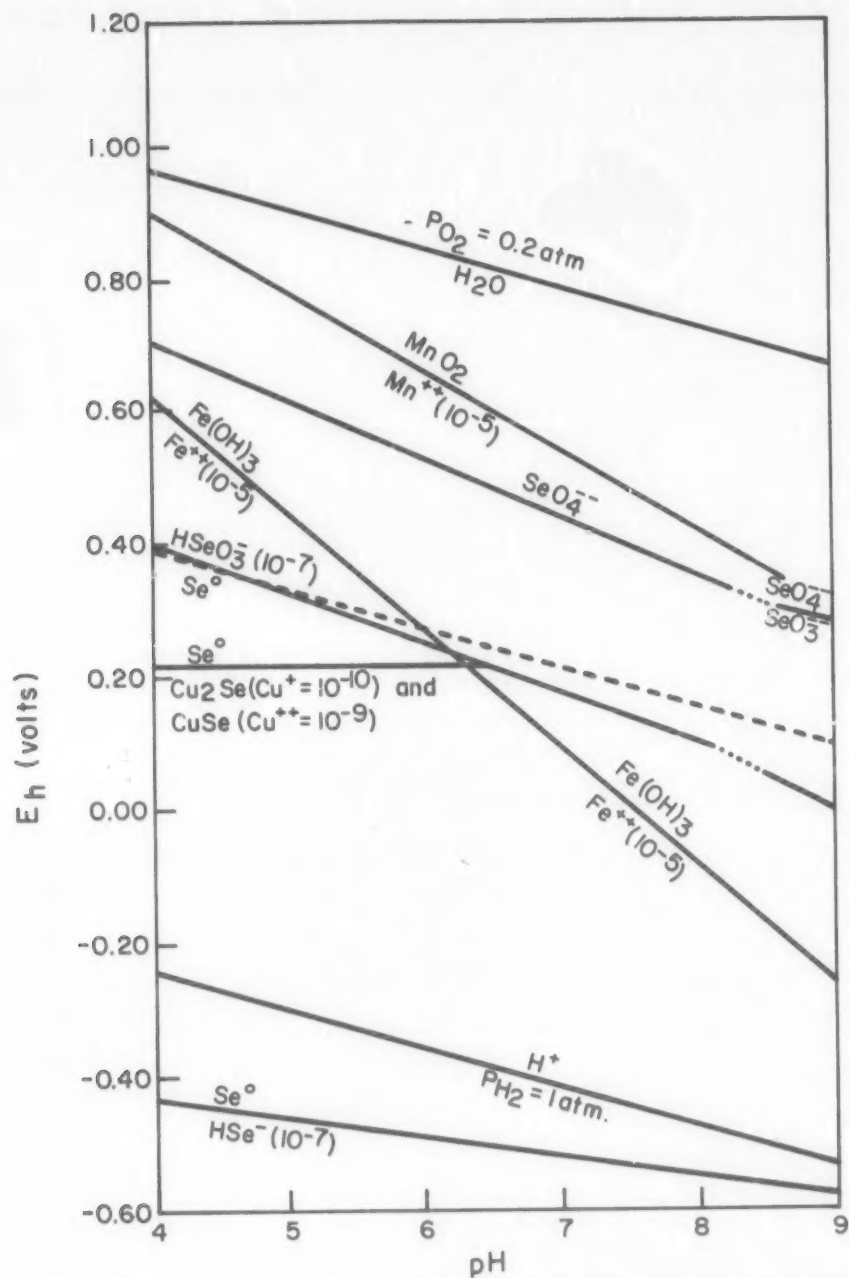


Figure 6.18. The oxidation-reduction potentials of selenium couples and some redox couples that could affect oxidation state of selenium in soils as a function of pH. (Dashed line is Pearsall's (1938) dividing line between oxidized and reduced soils.) (From Geering et al., 1968.)

drawn the $\text{Se}^\circ/\text{Cu}_2\text{Se}$ and CuSe , H^+/H_2 , and the $\text{Se}^\circ/\text{H}_2\text{Se}$ couples. The Eh values of the respective couples were calculated from the standard oxidation potentials given by Latimer [(1952)] and the dissociation constants [Sillen and Martell (1964)] of H_2SeO_4 , H_2SeO_3 and $\text{H}_2\text{SeO}_{\text{aq}}$ and the solubility products of Cu_2Se and CuSe [Buketov et al. (1964)]

"The activities of the various ion species in solution were selected from values reported in the literature. The values for Mn^{2+} and Fe^{2+} are maximum values reported by Leeper, while the activity for Se ions is an average, selected by Lakin (1961). The Cu^{2+} activity value is based on soil solution data reported by Hodgson and Geering, and the Cu^+ activity is a calculated value to allow the $\text{Se}^\circ/\text{Cu}_2\text{Se}$ couple to be represented by the same line as the $\text{Se}^\circ/\text{CuSe}$ couple.

"[...] one can see the regions of Eh and pH where one might expect to find one or another valence state of Se existing in the soil solution. In the region between the lines drawn for the $\text{O}_2/\text{H}_2\text{O}$ couple and the $\text{SeO}_4^{2-}/\text{SeO}_3^{2-}$ couple, one might expect essentially all of the Se in solution to be in the selenate form. Between the $\text{SeO}_4^{2-}/\text{SeO}_3^{2-}$ and $\text{SeO}_3^{2-}/\text{Se}^\circ$ lines, SeO_3^{2-} would be expected. Between the $\text{SeO}_3\text{Se}^\circ$ and the H^+/H_2 lines, only elemental Se and possibly some heavy metal selenides would be expected. No H_2Se by itself would be expected to exist in soils, except either in a metastable state or in concentrations very much less than 10^{-7}M , inasmuch as this redox couple falls even below the H^+/H_2 couple.

"While the redox potential of a soil may indicate what to expect regarding the valence state of Se in a soil, it yields little information about the kinetics or rates of conversion from one oxidation state to another. Experiments and observations with pure systems in the laboratory indicate that the rates of transformation of SeO_3^{2-} to SeO_4^{2-} and vice versa are relatively sluggish [Rosenfeld and Beath (1964)], whereas the rate of transformation of SeO_3^{2-} to Se° proceeds very readily. On the other hand, the oxidation of Se° to SeO_3^{2-} is very difficult to effect, unless Se° is finely dispersed

[Schulek and Koros (1960)]."

The paper by Geering et al. (1968) provides an excellent review and background of the solubility and redox criteria for the possible forms of selenium in soils and possible mechanisms of attenuation of Se as defined in the manuscript. Another paper concerning Se in soils is that of Brown and Carter (1969), who studied the leaching of added Se from alkaline soils as influenced by sulfate. Their leaching solutions for soil columns were water and gypsum solution.

ZINC

Zinc occurs in abundance in the earth's crust and exists only in the +2 oxidation state. Unlike cadmium, mercury, and lead, it is essential to most biological systems, including those of human beings. Also, unlike Cd, Hg, and Pb, it is not toxic in trace amounts. A few organisms, however, find it toxic at low levels. Since there is little tendency for Zn polymer formation, its hydrolysis chemistry is relatively simple. Such species as Zn(OH)^+ , Zn(OH)^{3+} are common. In very basic solutions zincates, Zn(OH)^{2-} , appear, Baes and Mesmer (1973).

Zinc oxide, ZnO , $\text{Zn(OH)}_2(\text{aq})$, and Zn(OH)_3^- stabilities are not precisely established. ZnO , though is the stable phase of zinc. Davies and Staveley (1972) and Schindler et al. (1964) have established the solubility of the most stable of the zinc hydroxides E-Zn(OH)_2 .

Zinc (Zn^{2+}) forms slowly soluble precipitates with carbonate, sulfide, silicate and phosphate ions. Hem (1970) and Stumm and Morgan (1970) have stressed the immobilization of the Zn silicates and carbonates in waters and soils. In waters which are carbonated (CO_2) Schindler et al. (1964) have reported the occurrence of $\text{Zn}_4(\text{OH})_6(\text{CO}_3)_2$ and ZnCO_3 .

Benson (1966), who studied the mobility of Zn in eight Washington soils, found that Zn is retained well in the upper part of the 2 cm x 75 cm soil columns when leached with the equivalent of 2 feet of water after

applying Zn at a rate of 0.2 g Zn/cm^2 . Six of the 8 soils were fine sandy loams; one was a fine sand, and one was a loam. Clay content was low. Applications of Zn salts to the soils resulted in a high Zn concentration in the upper few centimeters (5-10 cm). Zinc and K were shown to be competitive for exchange positions. Mobility of Zn in these soils may be expected because of their coarse sandy texture, generally low organic matter, and low clay content. Zinc was precipitated at or near the surface in the soil containing "free" calcium carbonate or lime. The same was true for the soil highest in organic matter.

Zinc may be retained in soils in excess to the exchange capacity. Bingham et al. (1964) explain the immobilization mechanism in terms of precipitation of Zn(OH)_2 rather than by assuming the formation and adsorption of complex ions Zn(OH)^+ . On the other hand, Tiller et al. (1962) suggest that the linear relationship they found in a great number of soil-water systems between the quality/intensity ratio of Zn and the soil pH could be accounted for only on a basis of the predominance of Zn(OH)^+ .

Only a part of the Zn adsorbed to soils can be removed with neutral salt. Jones et al. (1936) and Hibbard (1940), studying Zn adsorption in Florida and California soils, respectively, found that only acid extraction can remove this tightly bound Zn in soils. Perhaps there is a highly specific adsorption or complexing mechanism in soils for Zn. In a review of heavy metals and radio-nuclides in soils, Tiffin et al. (1973) makes the following statement concerning Zn retention:

"... a significant portion of Zn on montmorillonite, kaolinite and four soils was not readily extractable against N NH_4 -acetate, but it could be removed with acid. The smaller the amount of Zn that was added to the soil or clay, the larger was the fraction that was only exchangeable by acid, Nelson and Melsted (1955). The same was found for Cu, Peach (194). In both cases, the nonremovable fraction varied in size with pH and increased in size with time, Brown (1950). Clark and Graham (1968) observed a strongly increasing

diffusivity with increasing Zn concentration in sand, loams and clays at pH 5.0. They ascribed this partly to the greater fraction of Zn that is specifically adsorbed at the lower concentrations. From the relationship between diffusivity and distribution coefficient they concluded that some of the adsorbed Zn diffused at a significant rate by surface migration, Clark and Graham (1968).

"The rate of immobilization of Zn because of adsorption by montmorillonite followed first-order kinetics, Nelson and Melsted (1955). Zinc was found to be more strongly bound by montmorillonite than by attapulgite, and more Zn was available to plants from attapulgite containing high-pH rendzina soils than from soils containing montmorillonite, Navrot and Gal (1971). In comparison of calcite and magnesite in soil, Zn showed greater affinity for magnesite, in agreement with calculated ion geometry, Jurinak and Bauer (1956). Immobilization of Co and Zn by clay mineral adsorption followed a Freundlich type isotherm, with reactivity decreasing in the order hectorite > vermiculite > montmorillonite > holloysite > kaolinite for underground material, and muscovite talc > biotite = vermiculite > pyrophyllite for ground material, Tiller and Hodgson (1962). The particle size distribution of primary and secondary clay minerals have important effects on the mobility of trace metals in soil."

Zinc carbonate (ZnCO_3) and Zn(OH)_2 are reported by Norvell and Lindsay (1969) to be $\sim 10^5$ times more soluble than the Zn-soil complex responsible for fixing Zn in five soils. Furthermore, the solubility of Zn species in equilibrium with soil Zn (Figures 6.19 and 6.20) is seen to be Zn^{2+} below pH 7.7, and above this pH the neutral species $\text{Zn(OH)}_2(\text{aq})$ predominates. The solubility of $\text{Zn}_3(\text{PO}_4)_2$ is compared to ZnCO_3 , Zn(OH)_2 , and soil Zn in Figure 6.21. This seems to indicate phosphate may not be the element that is particularly significant in inducing Zn deficiency in soils as has often been suggested.

SOLUBILITY OF Zn MINERALS

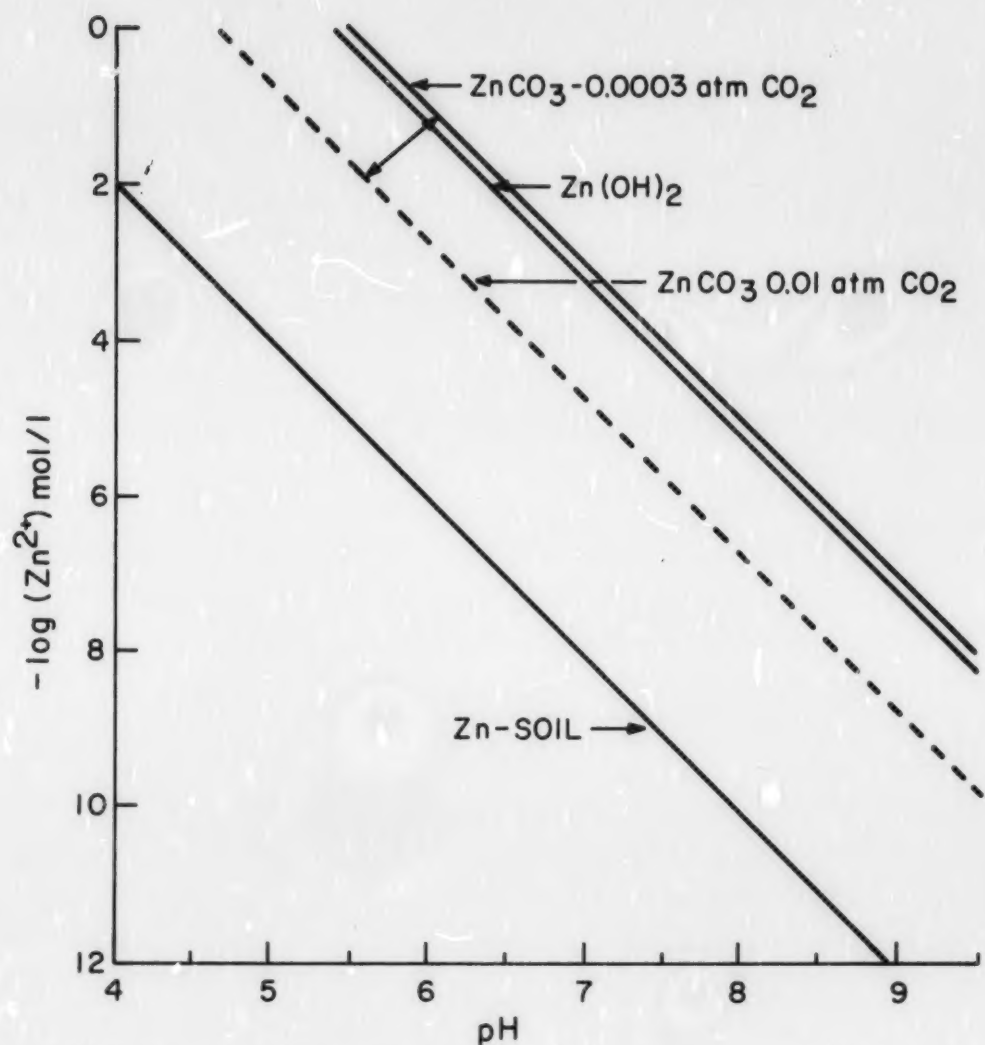


Figure 6.19. The solubility of various Zn minerals compared to the solubility of Zn in soils. (From Lindsay, 1972.)

Zn SOLUBILITY IN SOILS

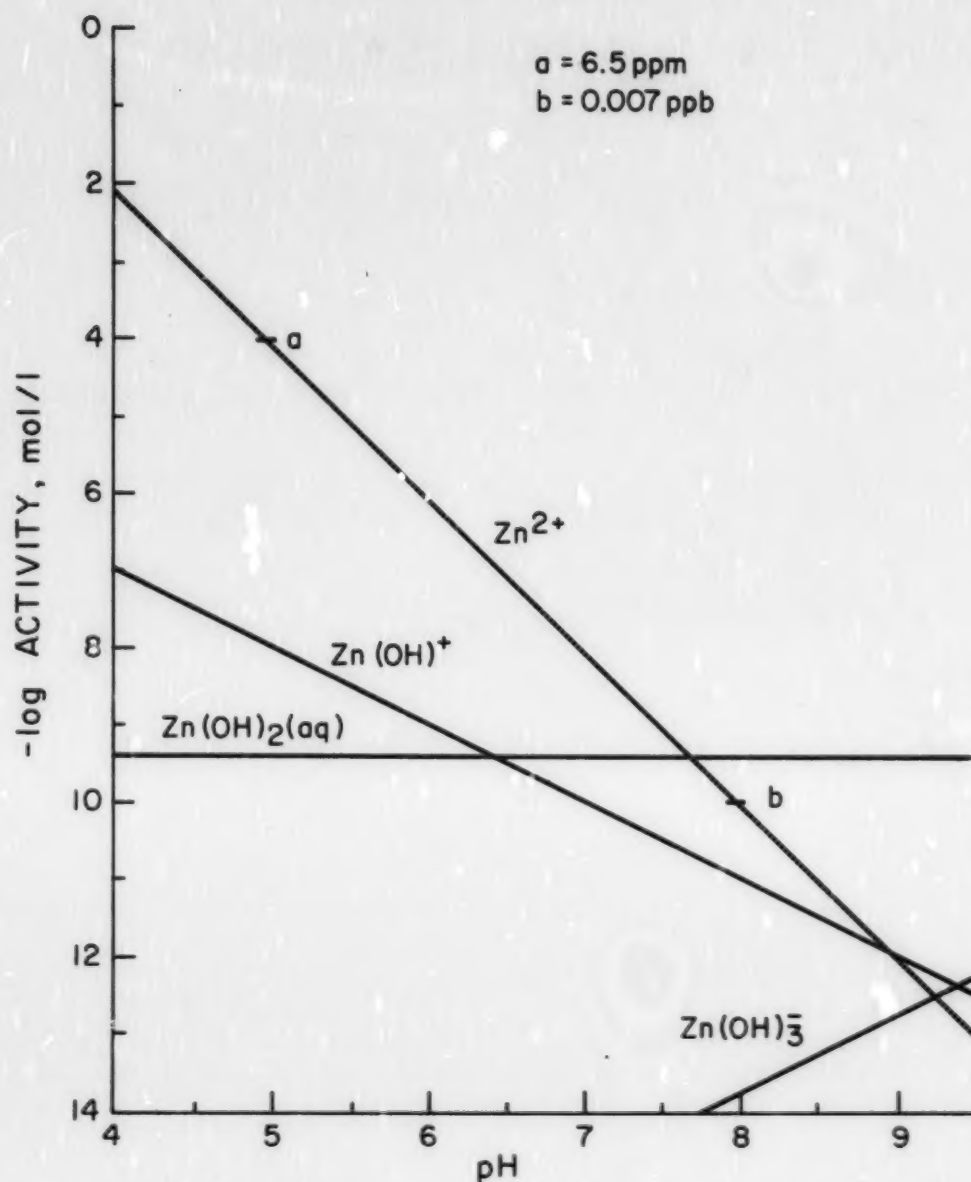


Figure 6.20. Soluble Zn species in solution in equilibrium with soil Zn.
(From Lindsay, 1972.)

SOLUBILITY OF Zn COMPOUNDS

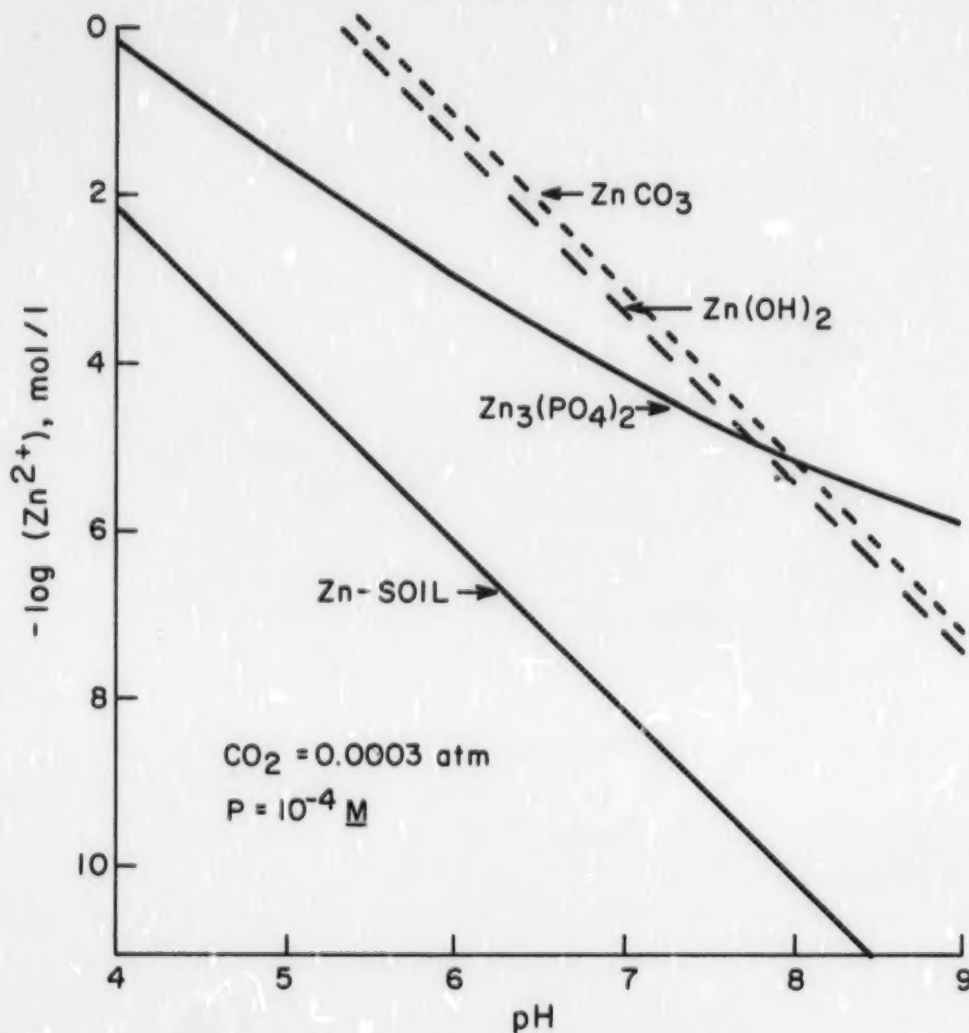


Figure 6.21. The solubility of $\text{Zn}_3(\text{PO}_4)_2$ compared to that of other Zn minerals and soil Zn. (From Lindsay, 1972.)

SECTION VII

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SECTION VIII

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APPENDIX A

POLLUTANT ATTENUATION RESEARCH AT THE UNIVERSITY OF ARIZONA¹

In a research project, directed by W.H. Fuller at The University of Arizona, the factors which attenuate contaminants (limit contaminant transport) in leachate from municipal solid waste landfills were examined. Although the work was strongly oriented toward problems with disposal of strictly municipal wastes, the impact of co-disposal of municipal and hazardous wastes was also considered. This project strongly emphasized the influence of soil and contaminant properties on migration.

The project was concerned with contaminants normally present in leachates from municipal solid waste landfills and with contaminants that are introduced or increased in concentration by co-disposal of hazardous wastes. These contaminants are: arsenic, beryllium, cadmium, chromium, copper, cyanide, iron, mercury, lead, nickel, selenium, vanadium, and zinc. The objectives of the project were to identify:

1. Soil factors that exert the greatest influence on contaminant migration.
2. Intrinsic mobility of contaminants and their properties which influence migration (e.g., oxidation state, compounds).

Eleven soils representative of 7 major orders were collected throughout the U.S. at depths to avoid organic matter in surface layers which would not be typical of soils below fills. They range in pH from 4.2 for the Ultisol, Wagram loamy sand, to pH 7.8 for the alkaline Aridisols, Anthony

¹"Investigation of Leachate Pollutant Attenuation in Soils," Contract 68-03-0208, Solid and Hazardous Waste Research Division, U.S. EPA Municipal Environmental Research Laboratory, Cincinnati, Ohio 45268.

sandy loam and Mohave_{Ca} clay loam. The clay ranges from 3 to 61% and cation exchange capacity (CEC) from 2 to 37 meq/100g. Two Mohave soils were included (because the presence of lime varies with depth), providing an opportunity to compare two genetically similar soils, one with and the other without lime. Physical and chemical characteristics of the soils are summarized in Table A-1.

The simulated municipal landfill leachate used in the study was generated in a 3,800 liter septic tank (Figure A-1) filled with representative municipal refuse (Table A-2). To insure uniformity, a pump was connected to the outlet to recirculate leachate back through the solid waste fill. Clear leachate was withdrawn from the bottom of the tank under high CO₂ pressure and in the exclusion of air (Korte et al., 1976). The characteristics of the leachates used in this research are shown in Table A-3.

The leachate was analyzed repeatedly until concentrations of most constituents reached near steady state. Atomic adsorption spectrometry was used to analyze for Fe, Mn, Zn, Cu, Ni, Cr, Pb, Co, Cd, Al, and Mg. Na, K, and Ca were measured by flame emission. Si, Cl, NO₃, NH₄, PO₄, and COD were measured by standard colorimetric procedures. The pH was measured in the field at the tank outlet and electrical conductivity (for dissolved solid evaluation) was measured in the laboratory. The composition of the solution is within the range for natural landfill leachates (Garland and Mosher, 1974).

Since no industrial wastes were included in the tank, the content of trace elements is low relative to that of mixed municipal and industrial wastes. This made it advantageous to "spike" or add to the leachate the specific trace element needed for study of migration characteristics.

Where spiked leachates were used, the pH was adjusted with HCl to 5.0, to facilitate handling and retard precipitation of dissolved ions, then spiked with the element of interest to a concentration of 70-120 ppm. These concentrations exceed that which might be expected for strictly municipal landfill leachates but resemble what might be found in mixed municipal-

TABLE A-1. SOME CHARACTERISTICS OF THE SOILS USED IN RESEARCH AT THE UNIVERSITY OF ARIZONA

Series	Order [†]	Soil Paste pH	Cation exchange capacity $\frac{\text{meq}}{100\text{g}} \times \frac{1}{2}$	Electrical conductivity of extract $\frac{\mu\text{hos}}{\text{cm}} \times \frac{1}{225}$	Column bulk density $\frac{\text{g}}{\text{cm}^3}$	Surface Area $\frac{\text{m}^2}{\text{g}}$	Free Iron oxides %	Total Mn ppm	Texture [*]			Major Clay Minerals ^{**}
									Sand %	Silt %	Clay %	
Wagram	Ultisol	4.2			1.89	8.0	0.6	50	88	8	4	Kaolinite, Chlorite
Ava	Alfisol	4.5	19	157	1.45	61.5	4.0	360	10	60	31	Vermiculite, Kaolinite
Kalkaska	Spodosol	4.7	10	237	1.53	8.9	1.8	80	91	4	5	Chlorite, Kaolinite
Davidson	Ultisol	6.2	9	169	1.89	51.3	17.0	4100	19	20	61	Kaolinite
MoTokai	Oxisol	6.2	14	1262	1.44	67.3	23.0	7400	23	25	52	Kaolinite
Chalmers	Mollisol	6.6	26	288	1.60	125.6	3.1	330	7	58	35	Kaolinite, Gibbsite
Nicholson	Alfisol	6.7	37	176	1.53	120.5	5.6	950	3	47	49	Montmorillonite, Vermiculite
Fanno	Alfisol	7.0	33	392	1.48	122.1	3.7	280	35	19	46	Vermiculite
Mohave	Aridisol	7.3	10	615	1.78	38.3	1.7	825	52	37	11	Montmorillonite, Mica
Mohave ^{Ca}	Aridisol	7.8	12	510	1.54	127.5	2.5	770	32	28	40	Mica, Kaolinite
Anthony	Entisol	7.8	6	328	2.07	19.8	1.8	275	71	14	15	Mica, Montmorillonite
												Montmorillonite, Mica

[†] U.S. Department of Agriculture Comprehensive Soil Classification System.

^{*} U.S. Department of Agriculture System.

^{**} The dominant mineral is listed first
Sand, 2mm-0.05mm; Silt, 0.05mm-0.002mm; Clay, <0.002mm diameter

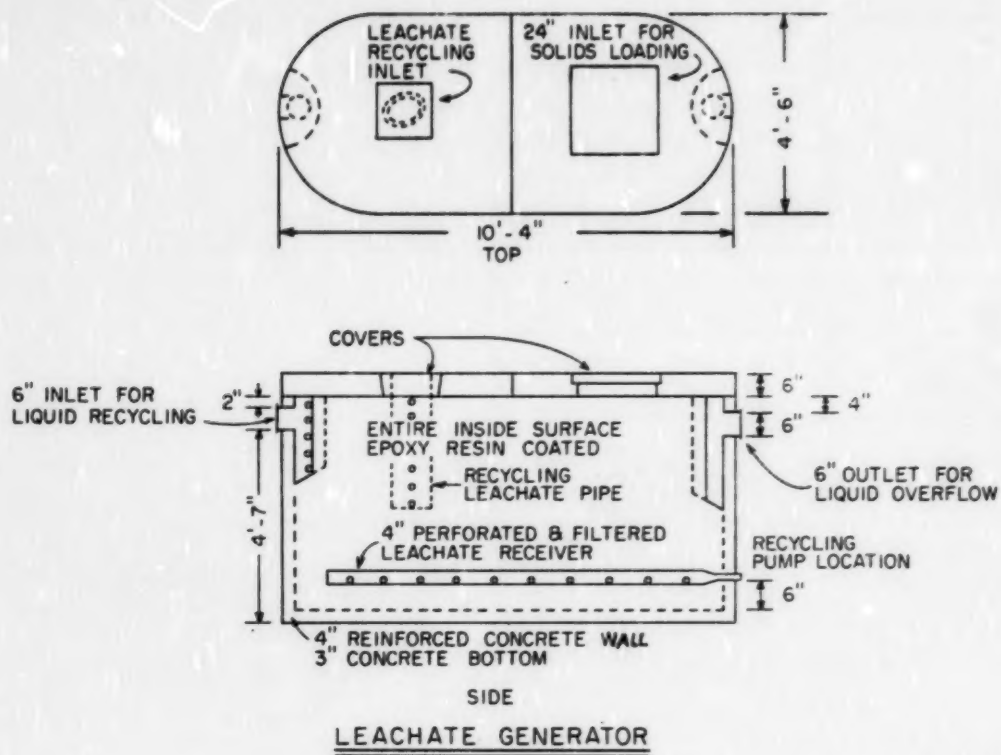


Figure A-1. Diagram of the municipal solid waste leachate generator.

TABLE A-2. PARTITIONING OF MATERIALS IN THE MUNICIPAL WASTE-TYPE LANDFILL USED TO GENERATE LEACHATE

Solid waste material	Amount loaded in 1000 gal. generator	
	lbs.	%
Paper (mostly newspaper)	1,400	45.7
Food waste	450	14.7
Garden waste	376	12.3
Plastic	34	10.2
Rubber	109	
Leather	60	
Textiles	109	
Metal (mostly cans)	187	6.1
Glass	177	5.8
Ash #59	127	4.1
Soil #68		
Calf manure	35	1.1

industrial waste leachates. Furthermore, these concentrations were necessary to assure migration through the soil columns in a reasonable period of time. The precipitation of Pb was retarded by further decreasing the pH of the solution to 3.0. Where possible, the appropriate chloride was used for spiking. Oxides were used for As, Cr, V, and Se, and a nitrate for Pb. The oxidation states for the elements were As^{+3} , Be^{+2} , Cd^{+2} , Cr^{+3} , Cu^{+2} , Hg^{+2} , Ni^{+2} , Pb^{+2} , Se^{+4} , and V^{+5} .

Other displacing solutions used for evaluating the contribution of the soil to the pool of soluble potentially hazardous elements were (a) aqueous H_2SO_4 adjusted to pH 3.0, (b) 0.025 M AlCl_3 plus 0.025 M FeCl_2 with enough HCl added to attain a pH of 3.0, and (c) deionized water.

One major problem encountered in this project was to preserve the leachate in its natural state for extended periods of time. The variation in analyses of landfill leachates (Brunner and Keller, 1972) reported in the

TABLE A-3. RANGES OF CONSTITUENTS DETECTED IN THE NATURAL LEACHATE
GENERATED FROM MUNICIPAL SOLID WASTE AND USED IN THE SOIL COLUMN RESEARCH

Constituent	Overall Range	Stabilized Range used in the research
	3/1/74 - 7/7/75	7/1/75 - 7/7/75
pH	6.6-6.8	6.6-6.8
	<u>ppm</u>	<u>ppm</u>
Al	bd1*	bd1
Ca	90-275	160-225
Cd	bd1	bd1
Co	bd1	bd1
Cr	bd1	bd1
Cu	bd1	bd1
Fe	48-120	60-120
K	150-950	850-950
Hg	bd1	bd1
Mn	0.6-1.8	0.6-1.8
Ni	bd1	bd1
NH ₄ -N	70-190	125-190
P	0.8-7.9	--
Pb	bd1	bd1
SiO ₃ -Si	19-31	20-25
Zn	0.1-3.4	0.4-0.65
Cl	93-3,900	780-**
COD	150-500	160-200
TDS	2,400-2,800	2,400-2,600

* bd1 - means below detectable limits; the bd1 for atomic adsorption method used, in $\mu\text{g}/\text{l}$ are: Cd = 0.005, Cr = 0.05, Co = 0.05, Cu = 0.05, Pb = 0.5, Ni = 0.05, Mn = 0.05, Zn = 0.005, Al = 0.5, and Fe = 0.05.

** Where leachates were spiked with a trace element to simulate levels more closely related to that of industrial waste streams, the Cl content may be as high as 5,000 ppm.

literature, leads to speculation that some of this variation is due to inadequate techniques for sample collection and preservation. Current practices in acidification of samples is not sufficient to keep all ions in solution. For example, acid will not prevent ferrous iron from being slowly oxidized and precipitated (Strumm and Morgan, 1970; and Cotton and Wilkinson, 1966). Simple acidification clearly is not acceptable for long-term research involvement with natural leachates.

In this project, samples were collected and maintained under CO_2 by first purging the collection vessel with the gas and then adding leachate while continuing to flush with CO_2 . Once the collection flask was filled, the CO_2 hose was withdrawn and the flask capped. For large samples and for preservation in the laboratory, CO_2 was constantly and vigorously bubbled through the leachate both during transport and storage.

Precautions were taken to preserve neutral natural leachates. Even momentary contact with the air resulted in precipitation and an increase in pH. When leachate was continually flushed with CO_2 , it could be preserved indefinitely without precipitation or changes in pH, color, and concentration of dissolved inorganic ions.

The soils were passed through a 2 mm sieve and then uniformly packed into 10 cm diameter x 20 cm PVC or 5 cm diameter x 10 cm PVC columns for irrigation studies. Packing into the columns was undertaken one centimeter at a time until full using a solid glass rod ~ 1 cm diameter for tamping. Bulk densities (Table A-1) for silt and clay soils exceeded 1.5 depending on the texture, and sands exceeded 2.0. These values were greater than those under natural field conditions and insured against channeling either internally in the soil body or along the sides of the columns.

The soil columns were saturated while inverted to exclude air and provide uniform wetting. Carbon dioxide was used to pump the solution to a constant head device where landfill leachate "spiked" with the potentially hazardous trace element was being studied. The height of the column was

adjusted to maintain as uniform a flux as possible. To retard stagnation in the manifold the solution could be recirculated back to the main reservoir. The leachate application and recirculation system is shown in Figure A-2.

The landfill leachate was continuously flushed with gas and the deionized H_2O , H_2SO_4 , and Al-Fe solutions with N_2 gas to keep the O_2 content at a minimum during the infiltration process. In the smaller columns (deionized H_2O and landfill leachate) the flow from each column was adjusted so that approximately one pore volume flowed from each column in 24 hours. The flow rate for the H_2SO_4 and Al-Fe solutions in the larger columns was maintained at $\sim$ one-half pore volume per day. Columns were leached until 15 or more pore volumes of water, natural leachate, or sulfuric acid solution had passed through the soil. The Al-Fe solution was allowed to flow until the effluent concentration of Al and Fe equalled that of the influent. Each sample was divided after collection so one part could be acidified to preserve it for trace element analysis and another for routine constituents.

Leaching was continued until one of three conditions were met; first, breakthrough (effluent conc. = influent conc.); second, steady state (unchanging or very slowly changing effluent concentration at value below that of influent); third, continued absence of the element after leaching.

At the conclusion of the leaching experiments the columns were segmented into ten sections of 1-cm each. Each segment was oven dried so that a material balance could be easily calculated and so that no variations in moisture content would be involved. Preliminary results showed that variations in extractability with dried versus saturated samples were slight.

Untreated soils were shaken with a solution containing the trace element to sorb the maximum amount on the soil. This soil was dried and used to determine optimum extraction times. Extractions were done with 0.1 N HCl and deionized water in a 1:10 soil solution rate. Samples were then centrifuged and the concentration of trace element in the extracting solution was measured by atomic absorption spectrometry. A material was calculated from the data and the percentage extracted was correlated to soil properties.

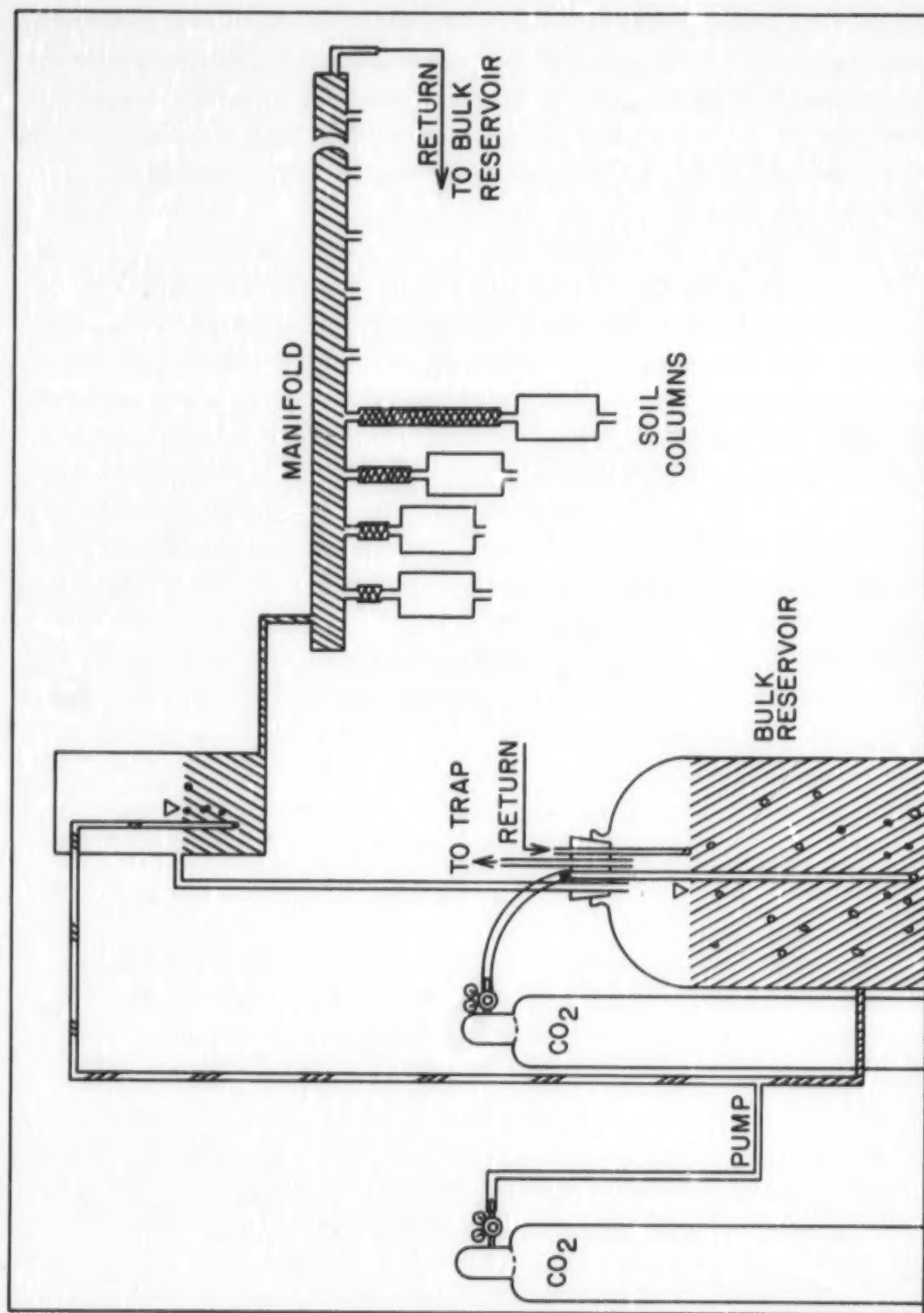


Figure A-2. System used at The University of Arizona for circulating and applying leachate anaerobically to soil columns.

Free iron oxides of the soils were determined by the method of Kilmer (1960), surface area by the method of Heilman et al. (1965), and manganese by modified procedure of Bernas (1968). For total analysis a sample size of 0.1 g of finely ground soil, 1 ml of aqua regia and 6 ml of HF were used for digestion. Boric acid (2.0 g) then was added and the sample diluted to a final volume of 50 ml.

The trace elements (As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) and Al, Fe, and Mn of the spiked leachates (influent) and soil column effluents were measured by atomic absorption spectrophotometry using standard procedures except for As, Se, and Hg. Because of the relatively high concentrations of these elements, the more specialized techniques of analysis, such as cold vapor mercury analysis (Hatch and Ott, 1968), and hydride generation of As and Se (Chu et al., 1972), were not required. Since these elements are subject to severe interference in atomic absorption analysis, chemical interferences were minimized by matrix adjustment. Lanthanum (1000 ppm) and K (100 ppm) were added to samples and standards alike to equalize the solution matrix for all samples. Non-atomic adsorption which was especially noticeable for Hg was measured with a H-continuum lamp (Varian Techtron), and subtracted from the sample reading.

Common ions (Ca, Mg, K, Na, Cl, $\text{NH}_4\text{-N}$, P, and Si) were determined by the standard U.S. EPA recommended methods (1971) and COD by the conventional Technicon Autoanalyzer method.

The pH values were measured using the glass electrode. Where pH, common ions, total dissolved solids were evaluated on water-saturated soils (soil-paste) and its extract, the method as recommended by the USDA (1954) was used as was the total dissolved solids (TDS) and cation exchange capacity (CEC).

Standard X-ray (Jackson, 1964) and mechanical analysis procedures (Day, 1965) were used to identify the $< 2\mu$ clay minerals and the particle size distribution of the soils.

Two types of variables were considered for the statistical analysis of the results: first, those representing soil properties -- clay, sand, percentage of free iron oxides, surface area, total manganese, pH, and electrical conductivity of the saturation extract -- and second, those measurements characterizing the migration and/or attenuation of the trace elements; mass adsorbed per gram of soil per milliliter of added leachate and maximum concentration. The mass balance for each soil column was calculated from daily measurements of the effluent and influent.

These data were first used to calculate a matrix of simple correlation coefficients (Korn and Korn, 1968) from which independent variables (clay, pH, etc.) having statistically significant relationships with the dependent variable (mass of element adsorbed per gram of soil per milliliter of added influent) were selected. To quantitatively decompose the effect of cross-correlation between independent variables (i.e., correlation between surface area and clay content) a stepwise multiple linear regression analysis (Efroymson, 1960) was performed using only independent variables which had statistically significant simple correlation coefficients. In this procedure a predicting equation of the form:

$$y = b_0 + b_1x_1 + b_2x_2 \dots + b_nx_n$$

where y = dependent variable

x_i = independent variables

b_i = coefficients

is derived by adding one variable at a time (stepwise) to the predicting equation, selecting as the next variable to be added, the one which most reduces the sum of squares deviation between observed and predicted y . The procedure is therefore a least squares analysis which is capable of "best fitting" linear combinations of independent variables to a dependent variable. The result is the evaluation and measurement of overall dependence of a variable on a set of other variables. This can be very useful for predictive purposes and also for providing the actual contribution of cross-correlated dependent variables.

The most significant findings were:

1. Soil properties most useful in predicting attenuation (retardation of migration) of contaminants by soils are:
 - a. Clay content
 - b. Content of hydrous oxides, primarily iron oxides
 - c. pH and content of free lime
 - d. Surface area per unit weight of soil
2. The mobility of the eleven contaminants studied may be classified as follows:
 - a. Most generally mobile - Cr, Hg, Ni
 - b. Least generally mobile - Pb, Cu
 - c. Mobility varies with conditions - As, Be, Cd, Se, V, Zn
3. Although the effect of soil solution flux (flow rate) was not thoroughly evaluated, attenuation appears to increase as flux decreases.

As a qualitative summary, Figures A-3 and A-4 present a ranking of the soils used in the project according to their attenuation properties and a ranking of the contaminants according to their mobility in the various soils. Separate rankings are given for contaminants present in the leachate as cations and as anions because of the differences in migration behavior shown in Tables 2 and 3. Note that every change in the ordering of soils when going from cations to anions involves a higher ranking for soils having a lower pH and/or a higher content of free iron oxides.

Based on the data analyses completed to date it is concluded that clay content, surface area, and content of hydrous oxides and free lime will be the soil properties most useful in selecting safe disposal sites for municipal and hazardous wastes. Additionally, the data suggests that use of lime and iron oxides should be examined as practical management tools for minimizing the movement of contaminants from landfills. Although information

INCREASING MOBILITY →

↑
INCREASING
ATTENUATION
CAPACITY

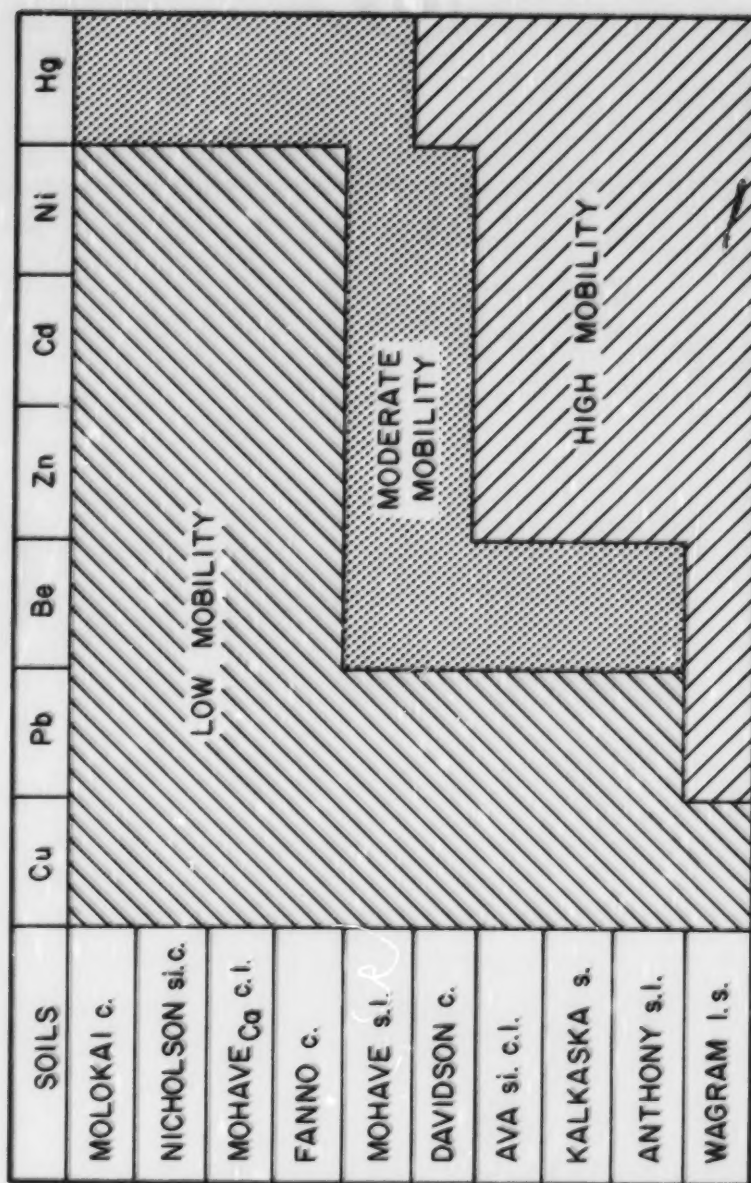


Figure A-3. Relative mobility of cations in soils used in the University of Arizona study.

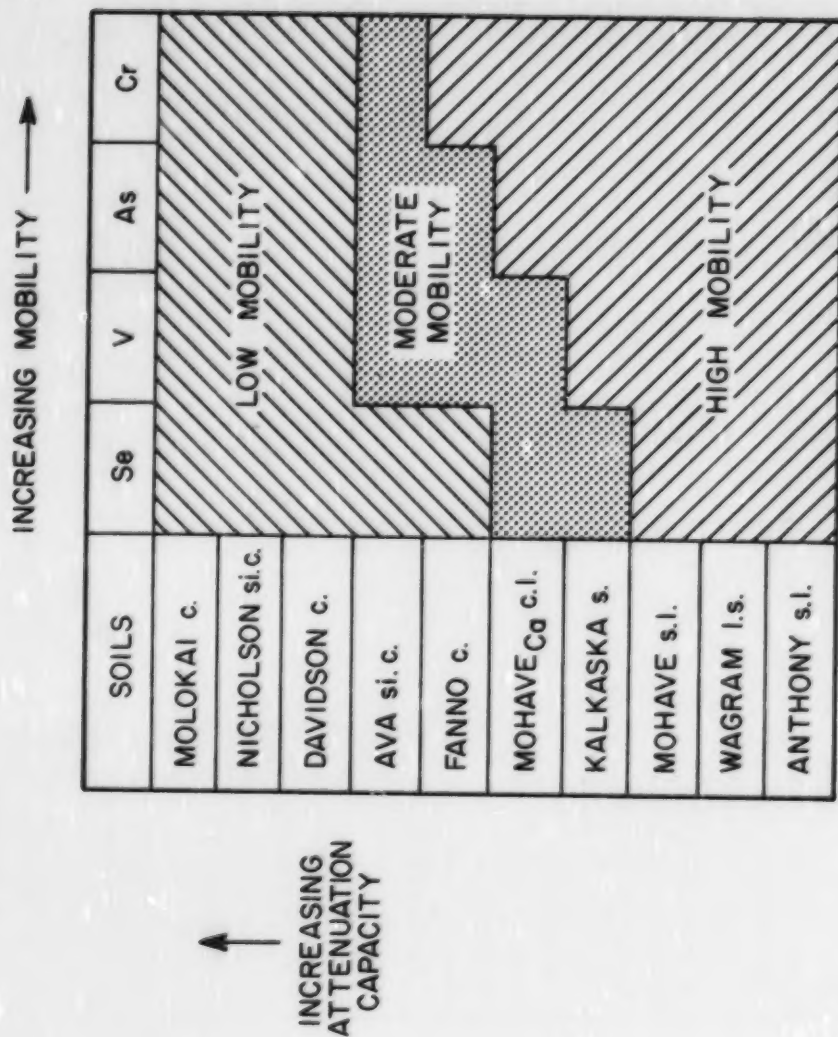


Figure A-4. Relative mobility of anions in soils used in the University of Arizona study.

about the relation between solution flux (flow rate) and attenuation is limited, it appears that at the low solution fluxes expected in unsaturated soils contaminant attenuation will be much greater than that observed in the saturated soils used in this study. This effect could also be used in management of landfills by lining with low permeability materials to reduce the rate of flow of leachate into soils below the landfill.

Further information on this project is contained in reports by Fuller (1975), Fuller and Korte (1976), and Korte et al. (1976).

APPENDIX B

SUPPLEMENTARY SOIL CLASSIFICATION INFORMATION

This appendix contains additional details on soil classification that will be helpful in relating this report to other reports on waste disposal, site selection, and soils research.

There are three systems under which soils are most likely to have been classified in the United States: The Unified Soil Classification System, the old (1938) U.S. Department of Agriculture System, and the present U.S. Department of Agriculture System.

The Unified Soil Classification System (USCS) serves engineering uses of soils and the criteria for soil types in the system are based on the grain (particle) size and response to physical manipulation at various water contents. Major divisions, soil type symbols, and type descriptions are shown in Table B-1. This is an abbreviated description of the system and does not include complete information on the use of the manipulation tests (liquid limit and plasticity index) in the classification.

The U.S. Department of Agriculture System (USDA) serves agricultural and other land management uses and the criteria for classification in the system are based on both chemical and physical properties of the soil. The USDA system in general use between 1938 and 1960 was based on soil genesis - how soils formed or were thought to have formed. The present USDA comprehensive soil classification system is based on quantitatively measurable properties of soils as they exist in the field. Although the present USDA system is incomplete and is being continually refined, it is generally accepted by U.S. soil scientists and its nomenclature is used in most of the

current literature. The present (1960) USDA system is described on pages 52 through 59. Table 4.4 on page 53 lists the Orders of the present system along with their approximate equivalents in the 1938 system. The geographic distribution of the Great Soil Groups of the old system is shown in Figure B-1; the geographic distribution of Orders and Suborders in the present system is shown in Figures B-2(A) and B-2(B). Additionally, Figure B-2(B) lists the approximate 1938 classification equivalents of the Suborders in the present system.

The part of the USDA classification which may be compared most directly with the soil types in the USCS system is soil texture (distribution of grain or particle size) and associated modifiers such as gravelly, mucky, diatomaceous, and micaceous. The size ranges for the USDA and the USCS particle designations (e.g. sand, gravel) are listed in Table B-2. The soil texture (USDA - sandy loam, silt loam, etc.) or the soil type (USCS - GC clayey gravel, SC clayey sand etc.) is based on the relative amounts of different sized particles in a soil. The USDA system for classifying soil texture is described on page 42 and in Figure 4.1 on page 43; an abbreviated description of the USCS classification is listed in Table B-1. An unpublished* correlation of the USCS and USDA systems on the basis of texture is presented in Tables B-3 and B-4. It should be emphasized that this correlation is not precise because texture is a high level (major) criterion in the USCS while texture is a low level (minor) criterion in the USDA system. A soil of a given texture can be classified into only a limited number of the 15 USCS soil types while in the USDA system, soils of the same texture may be found in many of the 10 Orders and 43 Suborders because of differences in their chemical properties or the climatic areas in which they are located.

* Personal communication. N. B. Schomaker, U.S. EPA Municipal Environmental Research Laboratory, Cincinnati, Ohio to W. H. Fuller, University of Arizona, Tucson, Arizona, Aug. 10, 1976.

TABLE B-1. MAJOR DIVISIONS, SOIL TYPE SYMBOLS, AND TYPE DESCRIPTIONS FOR THE UNIFIED SOIL CLASSIFICATION SYSTEM (USCS)

Major Divisions			Symbol	Description
<u>Coarse-grained soils</u> More than half of material is larger than No. 200 sieve size	<u>Gravels</u> More than half of coarse fraction is larger than No. 4 sieve size.	<u>Clean Gravel</u> (little or no fines)	GW	Well graded gravels, gravel-sand mixtures, little or no fines.
			GP	Poorly graded gravels or gravel-sand mixtures, little or no fines.
		<u>Gravels with Fines</u> (appreciable fines)	GM	Silty gravels, gravel-sand-silt mixture.
			GC	Clayey gravels, gravel-sand-clay mixtures.
	<u>Sands</u> More than half of coarse fraction is smaller than No. 4 sieve size.	<u>Clean Sands</u> (little or no fines)	SW	Well graded sands, gravelly sands, little or no fines.
			SP	Poorly graded sands or gravelly sands, little or no fines.
		<u>Sands with Fines</u> (appreciable fines)	SM	Silty sands, sand-silt mixtures.
			SC	Clayey sands, sand-clay mixtures.
<u>Fine-grained soils</u> More than half of material is smaller than No. 200 sieve size	<u>Silts and Clays</u> Liquid Limit is less than 50	ML	Inorganic silts & very fine sands, silty or clayey fine sands or clayey silts with slight plasticity.	
		CL	Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays.	
		OL	Organic silts and organic silty clays of low plasticity.	
	<u>Silts and Clays</u> Liquid Limit is greater than 50	MH	Inorganic silts, micaceous or diatomaceous fine sandy or silty soils, elastic silts.	
		CH	Inorganic clays of high plasticity fat clays.	
		OH	Organic clays of medium to high plasticity, organic silts.	
Highly Organic Soils		Pt	Peat & other highly organic soils.	
Notes: ML includes rock flour. The No. 4 sieve opening is 4.76 mm (0.187 in.); The No. 200 sieve opening is 0.074 mm (0.0029 in.)				

TABLE B-2. U.S. DEPARTMENT OF AGRICULTURE (USDA)
AND UNIFIED SOIL CLASSIFICATION SYSTEM (USCS) PARTICLE SIZES

USDA		USCS	
Particle	Size Range (mm)	Particle	Size Range (mm)
<u>Cobbles</u>	76.2 - 254.	<u>Cobbles</u>	>76.2
<u>Gravel</u>	2.0 - 76.2	<u>Gravel</u>	4.76 - 76.2
coarse gravel	12.7 - 76.2	coarse gravel	19.1 - 76.2
fine gravel	2.0 - 12.7	fine gravel	4.76 - 19.1
<u>Sand</u>	0.05 - 2.0	<u>Sand</u>	0.074 - 4.76
very coarse sand	1.0 - 2.0		
coarse sand	0.5 - 1.0	coarse sand	2.0 - 4.76
medium sand	0.25 - 0.5	medium sand	0.42 - 2.0
fine sand	0.1 - 0.25	fine sand	0.074 - 0.42
very fine sand	0.05 - 0.1		
<u>Silt</u>	0.002 - 0.05	<u>Fines*</u>	<0.074
<u>Clay</u>	<0.002	(silt & clay)	

* USCS silt and clay designations are determined by response of the soil to manipulation at various water contents rather than by measurement of size.

TABLE B-3. CORRESPONDING USCS AND USDA SOIL CLASSIFICATIONS

Unified Soil Classification System (USCS) Soil Types	Corresponding United States Department of Agriculture (USDA) Soil Textures
1. GW	Same as GP--gradation of gravel sizes not a criteria.
2. GP	Gravel, very gravelly* sand less than 5% by weight silt and clay.
3. GM	Very gravelly* sandy loam, very gravelly* loamy sand very gravelly* silt loam, and very gravelly* loam#.
4. GC	Very gravelly clay loam, very gravelly sandy clay loam, very gravelly silty clay loam, very gravelly silty clay, very gravelly clay#.
5. SW	Same - gradation of sand size not a criteria.
6. SP	Coarse to fine sand; gravelly sand ^Δ (less than 20% very fine sand).
7. SM	Loamy sands and sandy loams (with coarse to fine sand), very fine sand; gravelly loamy sand ^Δ and gravelly sandy loam ^Δ .
8. SC	Sandy clay loams and sandy clays (with coarse to fine sands); gravelly sandy clay loams and gravelly sandy clays ^Δ .
9. ML	Silt, silt loam, loam very fine sandy loam ^Φ .
10. CL	Silty clay loam, clay loam, sandy clays with <50% sand ^Φ .
11. OL	Mucky silt loam, mucky loam, mucky silty clay loam, mucky clay loam.
12. MH	Highly micaceous or diatomaceous silts, silt loams -- highly elastic.
13. CH	Silty clay and clay ^Φ .
14. OH	Mucky silty clay.
15. PT	Muck and peats.

*Also includes cobbly, channery, and shaly.

#Also includes all of textures with gravelly modifiers where >1/2 of total held on No. 200 sieve is of gravel size.

^ΔGravelly textures included if less than 1/2 of total held on No. 200 sieve is of gravel size.

^ΦAlso includes all of these textures with gravelly modifiers where >1/2 of the total soil passes the No. 200 sieve.

TABLE B-4. CORRESPONDING USDA AND USCS SOIL CLASSIFICATIONS

United States Department of Agriculture (USDA) Soil Textures	Corresponding Unified Soil Classification System (USCS) Soil Types
1. Gravel, very gravelly loamy sand	GP, GW, GM
2. Sand, coarse sand, fine sand	SP, SW
3. Loamy gravel, very gravelly sandy loam, very gravelly loam	GM
4. Loamy sand, gravelly loamy sand, very fine sand	SM
5. Gravelly loam, gravelly sandy clay loam	GM, GC
6. Sandy loam, fine sandy loam, loamy very fine sand, gravelly sandy loam	SM
7. Silt loam, very fine sandy clay loam	ML
8. Loam, sandy clay loam	ML, SC
9. Silty clay loam, clay loam	CL
10. Sandy clay, gravelly clay loam, gravelly clay	SC, GC
11. Very gravelly clay loam, very gravelly sandy clay loam, very gravelly silty clay loam, very gravelly silty clay and clay	GC
12. Silty clay, clay	CH
13. Muck and peat	PT

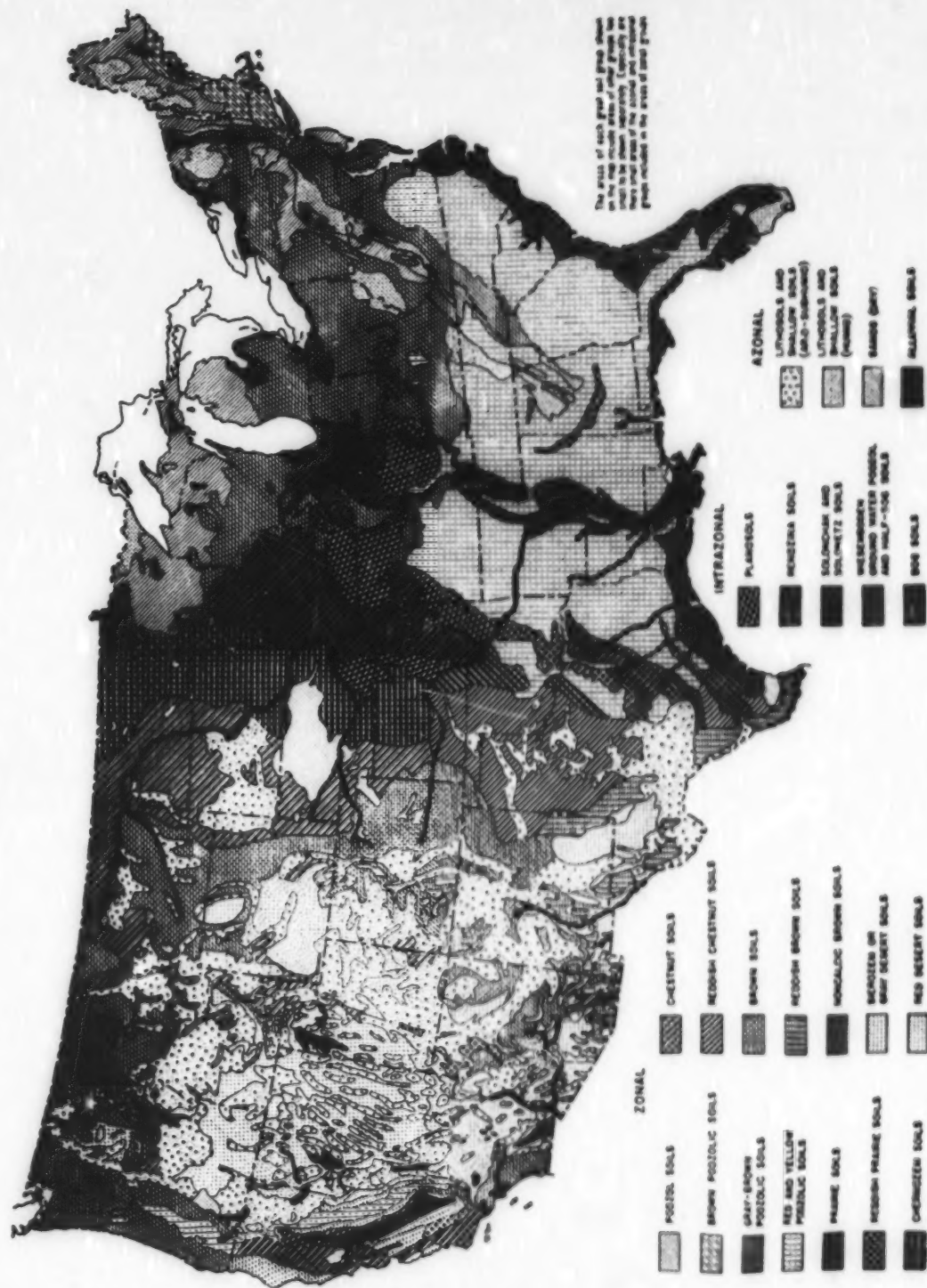


Figure B-1. Geographic distribution of Great Soil Groups in the 1938 U.S. Department of Agricultural Soil Classification System. (Courtesy of Soil Survey Division, U.S. Soil Conservation Service)



- ALFISOLS** . . . Soils with gray to brown surface horizons, medium to high base supply, and subsurface horizons of clay accumulation; usually moist but may be dry during warm season
- A1** AQUICULTS (seasonally saturated with water) gently sloping; general crops (if drained); pasture and woodland if undrained (Some Low-Humic Gray soils and Planosols)
- A2** BORALPTS (cool or cold) gently sloping; mostly woodland, pasture, and some small grain (Gray Eutric soils)
- A2S** BORALPTS steep; mostly woodland
- A3** UDALPTS (temperate or warm, and moist) gently or moderately sloping; mostly forest, corn, soybeans, small grain, and pasture (Gray-Brown Podzolic soils)
- A4** USTALPTS (warm and intermittently dry for long periods) gently or moderately sloping; range, small grain, and irrigated crops (Some Reddish Chestnut and Red-Yellow Podzolic soils)
- A5S** XERALPTS (warm and continuously dry in summer for long periods; moist in winter) gently sloping; to steep; mostly range, small grain, and irrigated crops (Nimblec Brown soils)
- ARIDISOLS** . . . Soils with pedogenic horizons, low in organic matter, and dry more than 6 months of the year in all horizons
- D1** ARGIDS (with horizon of clay accumulation) gently or moderately sloping; mostly range, some irrigated crops (Some Desert, Reddish Desert, Reddish-Brown, and Brown soils and associated Solonchaks soils)
- D1S** ARGIDS gently sloping to steep
- D2** ORTHIDS (without horizon of clay accumulation) gently or moderately sloping; mostly range and some irrigated crops (Some Desert, Reddish Desert, Sierrames, and Brown soils, and some Calcisols and Solonchaks soils)
- D2S** ORTHIDS gently sloping to steep
- ENTISOLS** . . . Soils without pedogenic horizons
- E1** AQUENTS (seasonally saturated with water) gently sloping; some grazing
- E2** ORTHENTS (loamy or clayey textures) deep to hard rock; gently to moderately sloping; range or irrigated farming (Regosols)
- E3** ORTHENTS shallow to hard rock; gently to moderately sloping; mostly range (Lithosols)
- E3S** ORTHENTS shallow to hard rock; steep; mostly range
- E4** PSAMMENTS (sand or loamy sand textures) gently to moderately sloping; mostly range in dry climates; woodland or cropland in humid climates (Regosols)
- HISTOSOLS** . . . Organic soils
- H1** FIBRISTS (fibrous or woody peats, largely undecomposed) mostly wooded or idle (Peats)
- H2** SAPRISTS (decomposed mucks) track crops if drained, idle if undrained (Mucks)
- INCERTISOLS** . . . Soils that are usually moist, with pedogenic horizons of alteration of parent materials but not of accumulation
- I1S** ANDRPTS (with amorphous clay or vitric volcanic ash and pumice) gently sloping to steep; mostly undrained, in Hawaii mostly sugar cane, pineapple, and range (Ando soils, some Tundra soils)
- I2** AQUPTS (seasonally saturated with water) gently sloping; if drained, mostly row crops, corn, soybeans, and cotton; if undrained, mostly woodland or pasture (Some Low-Humic Gray soils and Alluvial soils)
- I2P** AQUPTS (with continuous or sporadic permafrost) gently sloping to steep; woodland or idle (Tundra soils)
- I7** OCHREPTS (with thin or light-colored surface horizons and little organic matter) gently to moderately sloping; mostly pasture, small grain, and hay (Some Brown Acidic and some Alluvial soils)
- I3S** OCHREPTS gently sloping to steep; woodland, pasture, small grain
- I4S** UMIREPTS (with thick dark-colored surface horizons rich in organic matter) moderately sloping to steep; mostly woodland (Some Regosols)
- MOLLISOLS** . . . Soils with nearly black, organic-rich surface horizons and high base supply
- M1** AQUOLLS (seasonally saturated with water) gently sloping; mostly drained and farmed (Humic Gray soils)
- M2** BOROLLS (cool or cold) gently or moderately sloping; some steep slopes in Utah; mostly small grain in North Central States, range and woodland in Western States (Some Chernozems)
- M3** UDOLLS (temperate or warm, and moist) gently or moderately sloping; mostly corn, soybeans, and small grains (Some Brunas)
- M4** USTOLLS (intermittently dry for long periods during summer) gently to moderately sloping; mostly wheat and range in western part, wheat and corn or sorghum in eastern part, some irrigated crops (Chernozem soils and some Chernozems and Brown soils)
- M4S** USTOLLS moderately sloping to steep; mostly range or woodland
- MISOLLS** . . . Soils with accumulations of amorphous materials in subsurface horizons
- M5S** XEROLLS moderately sloping to steep; mostly range
- SPodosols** . . . Soils with accumulations of amorphous materials in subsurface horizons
- S1** AQUODS (seasonally saturated with water) gently sloping; mostly range or woodland; when drained in Florida, citrus and special crops (Gumud-Water Podzols)
- S2** ORTHODS (with subsurface accumulations of iron, aluminum, and organic matter) gently to moderately sloping; woodland, pasture, small grain, special crops (Podzols, Brown Podzolic soils)
- S2S** ORTHODS steep; mostly woodland
- ULTISOLS** . . . Soils that are usually moist with horizon of clay accumulation and a low base supply
- U1** AQUULTS (seasonally saturated with water) gently sloping; woodland and pasture if undrained, feed and truck crops if drained (Some Low-Humic Gray soils)
- U2S** HUMULTS (with high or very high organic-matter content) and-estly sloping to steep; woodland and pasture if steep, sugar cane and pineapple in Hawaii, truck and seed crops in Western States (Some Reddish-Brown Latertic soils)
- U3** UDULTS (with low organic-matter content; temperate or warm, and moist) gently to moderately sloping; woodland, pasture, feed crops, tobacco, and cotton (Red-Yellow Podzolic soils, some Reddish-Brown Latertic soils)
- U3S** UDULTS moderately sloping to steep; woodland, pasture
- U4S** XERULTS (with low to moderate organic-matter content, continuously dry for long periods in summer) range and woodland (Some Reddish-Brown Latertic soils)
- VERTISOLS** . . . Soils with high content of swelling clays and wide deep cracks at some season
- V1** UDERTS (cracks open for only short periods, less than 3 months in a year) gently sloping; cotton, corn, pasture, and some rice (Some Grumusols)
- V2** USTERTS (cracks open and close twice a year and remain open more than 3 months); general crops, range, and some irrigated crops (Some Grumusols)
- AREAS with little soil** . . .
- X1** Salt flats
- X2** Rockland, ice fields

Figure B-2(B). Legend for Fig. B-2(A) "Geographic Distribution of Orders and Suborders"